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Investigation of the relationship of the excited state geometry change and the solvent dependent fluorescence of 9-methyl anthroate

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THE INVESTIGATION OF THE RELATIONSHIP OF THE

EXCITED STATE GEOMETRY CHANGE AND THE SOLVENT

DEPENDENT FLUORESCENCE OF 9-METHYL ANTHROATE

by

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ABSTRACT

Due to a geometry difference, the polarity of the first
excited singlet state of 9-methyl anthroate is shown to be
greater than that of the ground state. This polarity difference
results in solvent dependent fluorescence properties for this
molecule. From the Stokes shift variations of 9-methyl
anthroate fluorescence in polar aprotic solvents, the excited
state dipole moment is 4.5 D larger than the ground state
value. In protic solvents, the Stokes shifts are larger than
in polar aprotic solvents indicating a large hydrogen bond
contribution to excited state solvation in the former solvents.

In non-polar and some polar aprotic solvents, the fluor-
escence quantum yield ($\emptyset_f$) of 9-methyl anthroate is greater
than that of anthracene. It is suggested that the first
excited singlet lies at an intermediate position between the
first and second triplet states. Thus, the intersystem crossing
process to either triplet is inhibited and the $\emptyset_f$ increases.

The $\emptyset_f$ of 9-methyl anthroate decreases with increasing
solvent polarity. This quenching effect is greatest in protic
solvents. Fluorescence lifetime and $\emptyset_f$ data indicate that the
quenching in protic solvents is the result of increased rates
of radiationless decay. A strong hydrogen bond interaction
between the solvent and the excited state inducing an increase
in the rate of internal conversion is the likely mode for non-
radiative decay in protic solvents.

To my parents, Mr. & Mrs. George Hoffman

whose hard work and continual sacrifice did not gain them
two Cadillacs, but did gain them two very appreciative children.

ACKNOWLEDGMENTS

I would especially like to thank Dr. T. C. Werner of the Union College Chemistry Department. It was largely through his never-ending patience, his timely suggestions and his open-door policy that this work was completed.

I would also like to thank Dr. Peter Frosch and Dr. John Sowa for their helpful discussions. My appreciation is also extended to the rest of the faculty of the Union College Chemistry Department for their teachings and moral support.

I also wish to express my thanks to the following people for their assistance on various aspects of this work. To Drs. Renata Cathou and James Bunting of Tufts Medical School for the use of their Ortec fluorescence lifetime equipment and for their aid in the analysis of the data, to Mr. Tom Porro of the Perkin-Elmer Corporation for supplying the corrected spectral data necessary for the generating of the spectra sensitivity curve, and to Mrs. Jackie Giacco for sacrificing her weekend and patience to painstakingly type this thesis.

Ronald M. Hoffman

Ronald M. Hoffman

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INTRODUCTION

A molecule has various electronic energy states due to the distribution of its valence electrons. Normally, a molecule is found in the lowest energy level which is called the ground state. The levels above the ground state are called the excited states; the energy difference between these various levels being quantized ($\Delta E = h\nu$). The electronic states in which all of the electron spins are paired are called singlet states, while the electronic states in which two of the electron spins are unpaired are called triplet states.

Superimposed on these electronic energy levels are vibrational energy levels. When a molecule absorbs electronic energy, it goes from the lowest vibrational level of the ground state to the various vibrational levels of an excited electronic state. In 10^{-11} to 10^{-13} seconds, the molecule loses the excess vibrational energy and returns to the lowest vibrational level of the first excited electronic state. From this excited electronic state, three processes can occur (Figure 1). In the first process, the molecule can lose the excess electronic energy to the environment in a radiationless pathway known as internal conversion (IC). In the second process, the molecule can go from the first excited electronic state, a singlet state, to the triplet state through a radiationless pathway known as intersystem crossing (IX). In the third process, the molecule can return to the ground state by emitting the excess electronic energy in a radiative pathway called fluorescence (F).

FIGURE 1.

Jablonski Electronic State Diagram

S_0 - Ground State (a singlet)

S_1 - First Excited Singlet State

T_1 - First Excited Triplet State

E - Direction of Increasing Energy

A - Absorption

IC - Internal Conversion

F - Fluorescence

IX - Intersystem Crossing

P - Phosphorescence
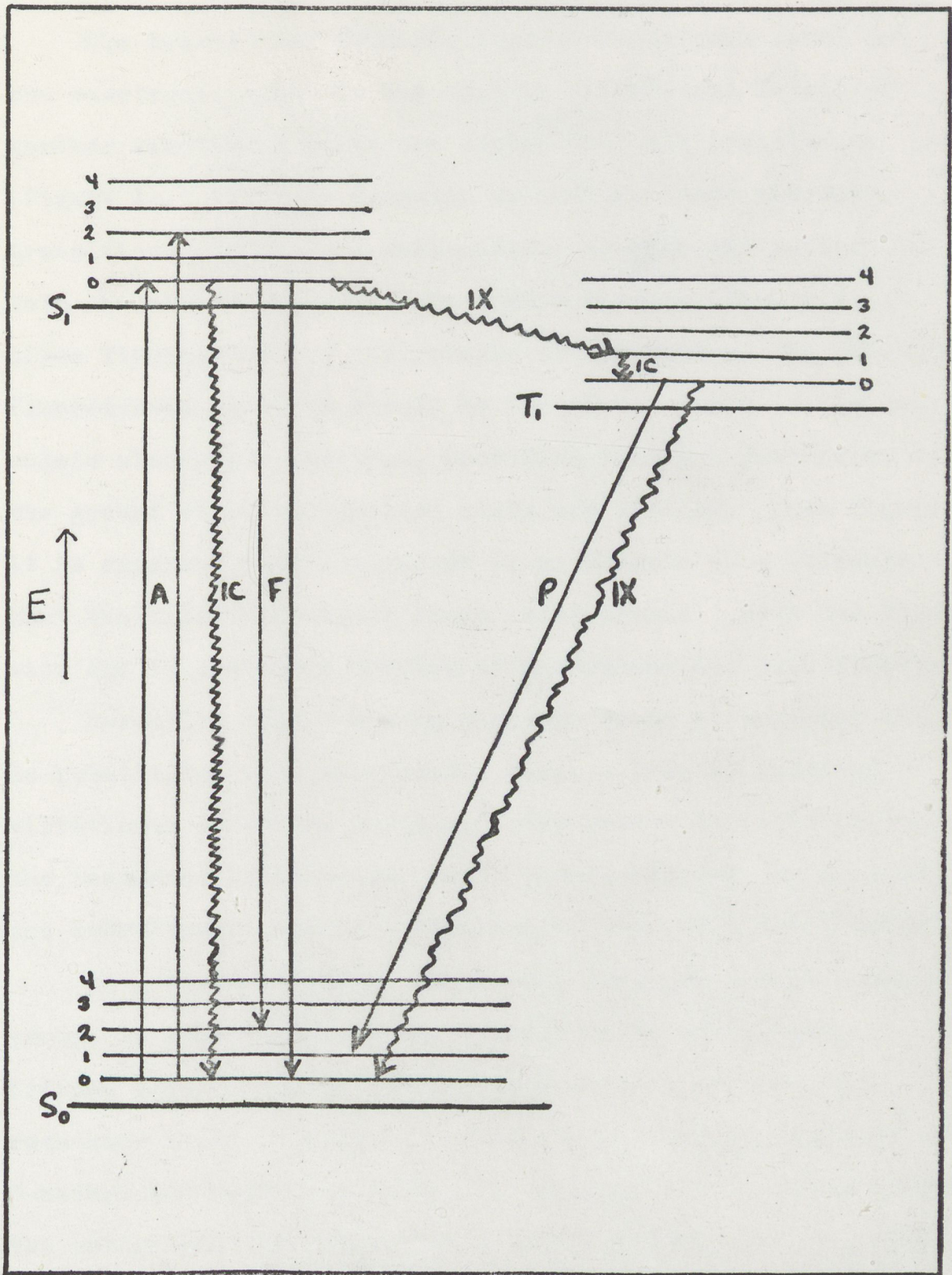
The transitions from the lowest vibrational level of one electronic state to the various vibrational levels of another electronic state are called vibronic transitions (Figure 1). For many aromatic molecules, these vibronic transitions result in a well-defined vibrational pattern in both the absorption and fluorescence spectra (Figure 2). Since fluorescense is the reverse of absorption, the classical fluorescence spectrum should be the mirror image of the molecule's absorption spectrum, providing that the geometries of the ground state and excited state are similar. From Figure 2, it is apparent that anthracene is an example of a molecule that exhibits this mirror image relationship. Both the absorption and fluorescence spectra of anthracene are very structured.

Normally, when a strong electron donor or acceptor group is substituted onto an aromatic ring, a loss in spectral vibrational structure results.[1] The reason for this is that the resonance interaction, which occurs between the ring and the substituent, causes a smearing of the vibrational pattern.

If a carboxyl group, which is a strong electron acceptor group, is substituted at the 9 position of anthracene, a diffuse absorption and fluorescence spectra due to this resonance would be expected. When the absorption spectrum of 9-methyl anthroate (9-COOCH$_3$) is examined, it is obvious that the anthracene-like structure remains (Figure 2). To understand this behavior, the geometry of the molecule must be mentioned. Norman, Ralph and others working with carboxylic

FIGURE 2.

Absorption and Fluorescence Spectra

of Anthracene and 9-COOCH$_3$ in Ethanol

———— - Absorption and Fluorescence Spectra
of Anthracene

(3.1 x 10^{-5} M, 1.00 cm cell)
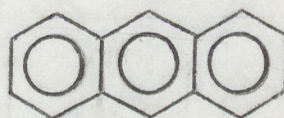
---+-- - Absorption and Fluorescence Spectra
of 9-COOCH$_3$

(3.1 x 10^{-5} M, 1.00 cm cell)
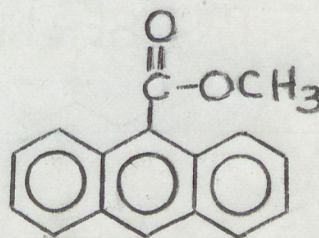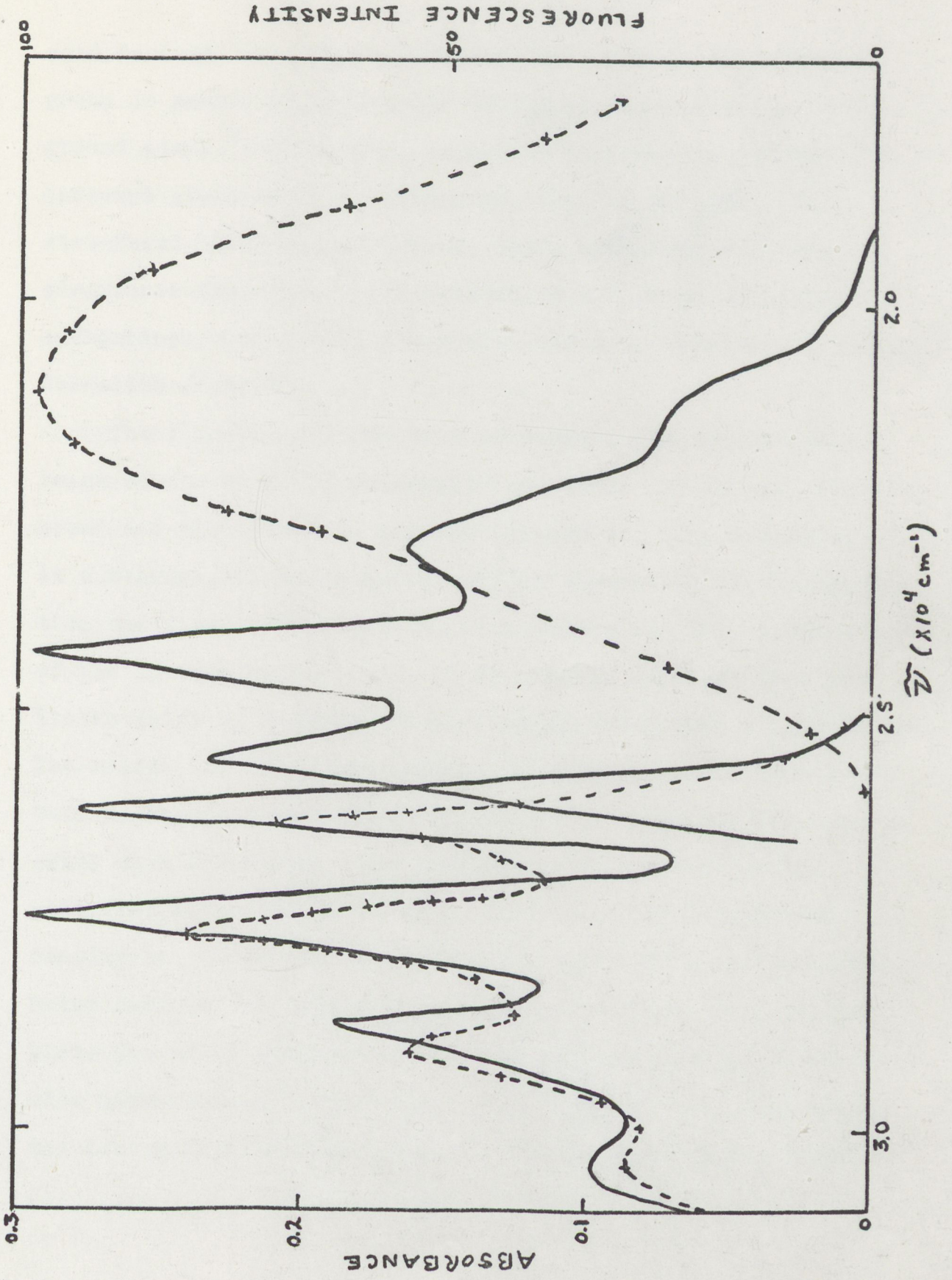
acid derivatives, have shown that the plane of the carboxyl group is nearly perpendicular to the anthracene rings in the ground state.[2] Therefore, resonance interaction between the carboxyl group and the anthracene rings is minimal. The structured absorption spectrum, then, indicates that the electronic transition is localized on the rings as it is in anthracene. Hence, the absorption spectrum retains its anthracele-like structure.

The fluorescence spectrum of $9-COOCH_3$ is not the mirror image of the $9-COOCH_3$ absorption spectrum. It is very diffuse, broad and highly Stokes shifted (Figure 2). The Stokes shift is a measure, in wavenumbers, of the separation of the absorption and fluorescence spectra of a molecule. From a comparison of the spectra in Figure 2, it is readily apparent that the Stokes shift of $9-COOCH_3$ is much larger than that of anthracene. The reason for this fluorescence behavior is that, upon excitation, the carboxyl group rotates until it approaches coplanarity with the rings. The anthracene ^1L_a transition is polarized along the 9, 10 axis and this shift in electron density on excitation introduces a degree of double bond character between the ring and the carboxyl carbon. The excited state therefore becomes more planer than the ground state. This hypothesis of a carboxyl group rotation was confirmed by the low temperature fluorescence spectra of anthracene deriva-

tives.

tives containing a carboxyl group at the 9 position.[1] At 77°K, in protic solvents, the rotation was blocked and the fluorescence spectra of the esters of 9-anthroic acid took on a structured anthracene-like appearance.

Due to this particular geometry change, there should be greater charge-transfer interaction between the ring and the carboxyl group in the excited state than in the ground state.[1] The excited state should, therefore, be more polar and its energy should show much more solvent dependence than that of the ground state. What is reported here is a study of the absorption and fluorescence spectra of 9-COOCH$_3$ as a function of solvent. The purpose was to evaluate the difference in the nature of the ground state and the lowest excited singlet state.

The carboxyl group substitution also affects other fluorescence properties of the parent hydrocarbon. In benzonitrile, the fluorescence efficiency for 9-COOCH$_3$ is about twice as large as the relatively solvent independent fluorescence efficiency of anthracene.[1] This is in contrast to the observation that carboxyl substitution generally inhibits fluorescence.[3] The values of the fluorescence efficiency and the fluorescence lifetimes (τ_f) for 9-COOCH$_3$ in ethanol are only about one-third of their respective values in benzonitrile.[1] In addition, there is a significant difference in the wavelength maximum of fluorescence in the two solvents.[1] From this solvent dependence

of the fluorescence efficiency and τ_f, the radiative and the
sum of the radiationless rate constants can be calculated.
Using this data, it is possible to comment on the modes of
the solvent induced reduction or quenching of 9-$COOCH_3$ fluor-
escence.

EXPERIMENTAL

I. Chemicals

Acetone, acetonitrile, benzonitrile, N,N-dimethyl-formamide, p-dioxane, ether, methyl formate, 2-propanol, 2,2,2-trifluoroethanol and carbon tetrachloride were Matheson Coleman and Bell Spectroquality solvents. Initially some of these spectral solvents were purified in the following manner: acetone and benzonitrile after standing over molecular sieves overnight, were distilled from P_2O_5, p-dioxane, after standing over potassium hydroxide overnight, was distilled from sodium metal, acetonitrile was distilled from P_2O_5, and 2-propanol was distilled from magnesium turnings. The spectral data obtained in these purified solvents were not significantly different from spectral data obtained in solvents taken directly from the bottle. Further purification of all spectral grade solvents was therefore unnecessary.

Methanol and benzene were Fisher Scientific Company Spectroanalyzed solvents.

The absolute ethanol used was obtained from U. S. Industrial Chemicals.

Deuterium oxide (99.8% minimum isotopic purity) was obtained from Diaprep Incorporated, Atlanta, Georgia.

Paraffin oil and trifluoroacetic anhydride were obtained from Matheson Coleman and Bell.

2-Chloroethanol, obtained from Eastman Kodak Company, was distilled immediately before use.

All other solvents were reagent grade or better, if possible, and used without further purification.

9-Methyl anthroate was prepared and purified by Dr. T. C. Werner from 9-anthroic acid using the method described by Moore and Reed.[4]

9-tert-Butyl anthroate was prepared from 9-anthroic acid by Alex Bodenstab following the procedure of Parish and Stock.[5]

9-Anthroic acid (99.5%) was obtained from Aldrich Chemical Company.

II. Instrumentation

All absorption spectra were recorded on a Cary Model 14 Spectrophotometer.

Fluorescence spectra were recorded on a Perkin-Elmer Hitachi-MPF-2A Spectrofluorometer which was uncorrected for spectral response. Correction factors for the Xenon source-excitation monochromator system were obtained with a rhodamine B quantum counter as described by Chen.[6] The correction for the response of the emission monochromator-detector side was made by determining a sensitivity curve from 380-580 nm. This was done by comparing the uncorrected emission spectra of 9-COOCH$_3$ in ethanol and in cyclohexane with corrected spectra of this

ester obtained under identical conditions on a corrected
spectral instrument at the Perkin-Elmer Corporation, Norwalk,
Connecticut. To compare these spectra, the relative intensities
versus wavelengths were obtained and plotted for each solvent.
The sensitivity curve was then determined by using the
following relations:

$R(\lambda)$ = relative intensity of uncorrected spectrum at λ

$C(\lambda)$ = relative intensity of corrected spectrum at λ

$S(\lambda)$ = sensitivity factor at λ

$$S(\lambda) = \frac{R(\lambda)}{C(\lambda)} \qquad (1)$$

Two different solvents, ethanol and cyclohexane, were used so
that a significant fluorescence signal could be measured from
380-580 nm. In cyclohexane, the fluorescence of $9\text{-}COOCH_3$
occurs mostly in the short wavelength region of the range
while in ethanol the fluorescence extends to the longer wave-
length region.

Once the sensitivity curve was produced, the uncorrected
emission spectra were corrected by using Equation 2.

$$C(\lambda) = \frac{R(\lambda)}{S(\lambda)} \qquad (2)$$

These corrections were done by computer. See Appendix II.

III. Fluorescence Quantum Yield and Lifetime Measurement

Fluorescence quantum yields (ϕ_f) were determined by
comparing the corrected sample spectrum to a corrected reference
spectrum using the following equation:

$$\phi_u = \phi_r \frac{n_u{}^2}{n_r{}^2} \frac{A_r}{A_u} \frac{F_u}{F_r} \qquad (3)$$

where r = reference, u = unknown, n = solvent refractive index, A = solution absorbance at the exciting wavelength(< 0.02, 1 cm cells), and F = the area under the corrected emission spectrum using the cut and weigh technique. The reference ϕ_f was from $9\text{-}COOCH_3$ in ethanol ($\phi_r = 0.18$ ref.[1]). Deoxygenation of solutions with $\phi_f > 0.20$ was accomplished by 5-6 freeze-pump-thaw cycles with subsequent sealing of the solutions in the cells under vacuum before the fluorescence was measured. For smaller ϕ_f values, the short fluorescent lifetimes prevented significant oxygen quenching. All reported ϕ_f values are the average of at least three independent determinations.

Fluorescence lifetimes were obtained with the Ortec Nanosecond Decay Time Fluorescence System. This instrument uses the monophoton technique.[6] The decay curves were deconvoluted and analyzed using the method of moments[7] in conjunction with an IBM computer. The best fit of the data was obtained by assumption of a single component decay. Solutions with lifetimes greater than 4 nS were deoxygenated and sealed as described above.

RESULTS

The spectral data, Stokes shift ($\tilde{\nu}_a - \tilde{\nu}_f$), fluorescence quantum yield ($\emptyset_f$), and some fluorescence lifetimes for 9-methyl anthroate in 28 solvents and solvent mixtures are summarized in Table 1.

The absorption spectra of this ester are anthracene-like in appearance; while the fluorescence spectra are very broad, diffuse bands. Only in cyclohexane does the fluorescence spectrum of the ester show slight vibronic structure. Because these spectra are structureless, the 0-0 fluorescence band could not be ascertained, so the fluorescence maxima are reported in Table 1. The Stokes shift ($\tilde{\nu}_a - \tilde{\nu}_f$) is usually defined as the distance, in wavenumbers, from the 0-0 absorption band to the 0-0 fluorescence band. However, since only the fluorescence maxima could be determined, the Stokes shift, for this work, is defined as the distance, in wavenumbers, from the 0-0 absorption band to the fluorescence maximum.

Figure 3 shows a plot of the Stokes shift versus the solvent polarity as indicated by Kosower Z values.[8] This plot indicates that as the solvent polarity increases, as reflected by the increasing Kosower Z values, the Stokes shift increases. The position of the absorption bands is seen to be relatively solvent independent (Table 1). This means that the increase in Stokes shift with increasing Z value is mostly the result of a shift of the fluorescence maximum towards lower energies with increasing solvent polarity.

TABLE 1.

Spectral Data for 9-COOCH$_3$ in Various Organic Solvents and Solvent Mixtures

Solvent	Z(a)	ϕ_f(e)	$\widehat{\nu}_a \times 10^{-4}$cm^{-1}(c)	$\widehat{\nu}_f \times 10^{-4}$cm^{-1}(d)	$(\widehat{\nu}_a - \widehat{\nu}_f) \times 10^{-3}$cm^{-1}	τ_f(nsec)
Ethanol (10%)	93.6	0.02	2.62	2.01	6.1	
" (20%)	92.6	0.03	2.62	2.02	6.0	
" (30%)	91.6	0.04	2.62	2.04	5.8	
" (40%)	90.5	0.06	2.62	2.04	5.8	
" (50%)	89.2	0.08	2.62	2.06	5.6	1.9 $\pm$1
" (60%)	87.9	0.09	2.62	2.07	5.5	
" (70%)	86.4	0.11	2.62	2.08	5.4	
" (80%)	84.8	0.13	2.62	2.09	5.3	
" (90%)	82.5	0.15	2.62	2.08	5.4	
" (100%)	79.6	0.18	2.62	2.11	5.1	4.1 $\pm$1
Dioxane (10%)	93.0	0.02	2.61	2.03	5.8	
" (20%)	91.4	0.03	2.61	2.04	5.7	
" (30%)	89.9	0.04	2.61	2.04	5.7	
" (40%)	88.4	0.07	2.61	2.06	5.5	

TABLE 1. (cont'd)

Solvent	Z(a)	ϕ_f(e)	$\tilde{\nu}_a \times 10^{-4}$ cm^{-1}(c)	$\tilde{\nu}_f \times 10^{-4}$ cm^{-1}(d)	$(\tilde{\nu}_a - \tilde{\nu}_f) \times 10^{-3}$ cm^{-1}	τ_f(nsec)
Dioxane (50%)	86.7	0.10	2.61	2.08	5.3	1.3 ± 1
" (60%)	85.0	0.14	2.61	2.08	5.3	
" (70%)	82.8	0.16	2.61	2.08	5.3	
" (80%)	80.2	0.22	2.61	2.11	5.0	
" (90%)	76.7	0.29	2.61	2.14	4.7	
" (100%)	55.4(b)	0.55	2.61	2.18	4.3	14.4 ± 0.5
Methanol	83.6	0.11	2.62	2.10	5.3	1.7 ± 1
Trifluoro-ethanol		0.02	2.64	2.05	5.9	
Isopropanol	76.3	0.24	2.62	2.11	5.1	
Acetonitrile	71.3	0.32	2.62	2.13	4.9	8.1 ± 0.5
Benzonitrile	65.5	0.65	2.59	2.14	4.5	12.7 ± 0.5
Acetone	65.7	0.44	2.62	2.15	4.7	12.9 ± 0.5
Benzene	54	0.64	2.61	2.17	4.4	14.1 ± 0.5
Cyclohexane	47(b)	0.68	2.62	2.21	4.1	13.1 ± 0.5

(a)   See Ref. 8

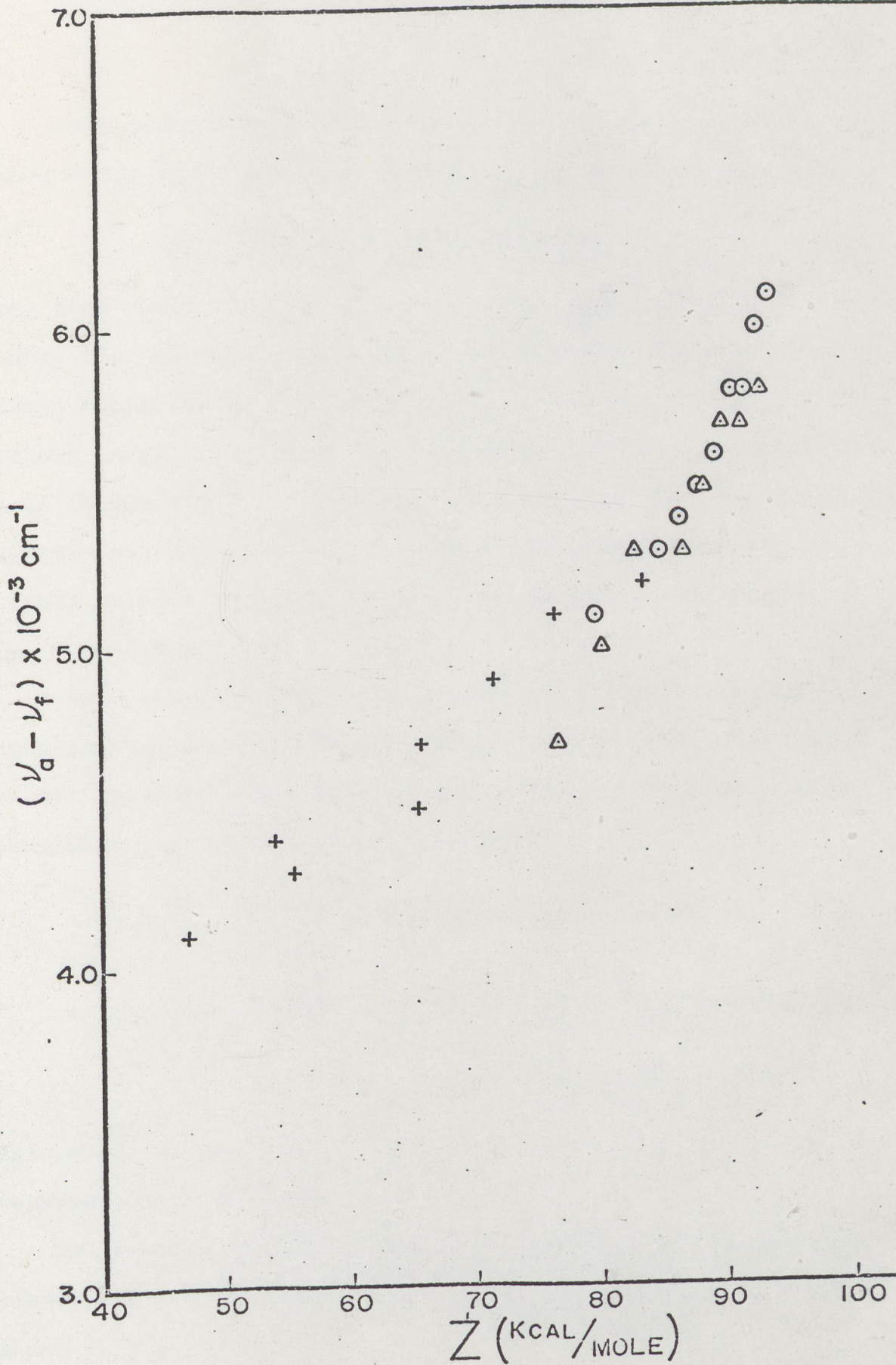(b)   Estimated from E_T values.   See Ref. 8

(c)   0-0 Absorption band

(d)   Fluorescence maximum

(e)   ± 10% accuracy

FIGURE 3.

The Stokes Shift of 9-COOCH$_3$ Fluorescence

as a Function of Kosower Z Value

⊙ - Ethanol - Water Mixtures

△ - Dioxane - Water Mixtures

+ - Pure Organic Solvents

The fluorescence quantum yield ($\emptyset_f$) of 9-COOCH$_3$ was also found to be solvent dependent. The $\emptyset_f$ is defined as:

$$\emptyset_f = \frac{\text{number of photon emitted}}{\text{number of photon absorbed}} \qquad (4)$$

and thus varies from zero to one. The plot in Figure 4 shows that $\emptyset_f$ values decrease with increasing solvent polarity, again indicated by Kosower Z values. The range of $\emptyset_f$ is rather large, going from approximately 0.70 in cyclohexane to 0.02 in 10% ethanol - 90% H$_2$O. In non-polar and in some polar aprotic solvents, the $\emptyset_f$ of 9-COOCH$_3$ is larger than the relatively solvent independent $\emptyset_f$ of unsubstituted anthracene ($\emptyset_f = 0.28$-0.36, ref. 9, 10).

From the $\emptyset_f$ and γ_f data reported in Table 1 and the equations below, the relative effects of the various solvents on the radiative (k_f) and the sum of the non-radiative rate constants ($k_{ic} + k_{ix}$) can be determined.

$$k_f = \frac{\emptyset_f}{f} \quad k_f = \text{fluorescence rate constant} \qquad (5)$$

$$(k_{ic} + k_{ix}) = \frac{k_f}{\emptyset_f} - k_f \quad k_{ic} = \text{internal conversion} \atop \text{rate constant} \qquad (6)$$

$$k_{ix} = \text{intersystem crossing} \atop \text{rate constant}$$

Values for k_f and ($k_{ic} + k_{ix}$) are given in Table 2 for ten representative solvents.

A close examination of Table 2 reveals that the solvents listed can be grouped into three categories based upon their capabilities to affect a change in the rate constants. The

FIGURE 4.

The Quantum Yield of 9-COOCH$_3$ Fluorescence

as a Function of Kosower Z Value

⊙ - Ethanol - Water Mixtures

△ - Dioxane - Water Mixtures

+ - Pure Organic Solvents
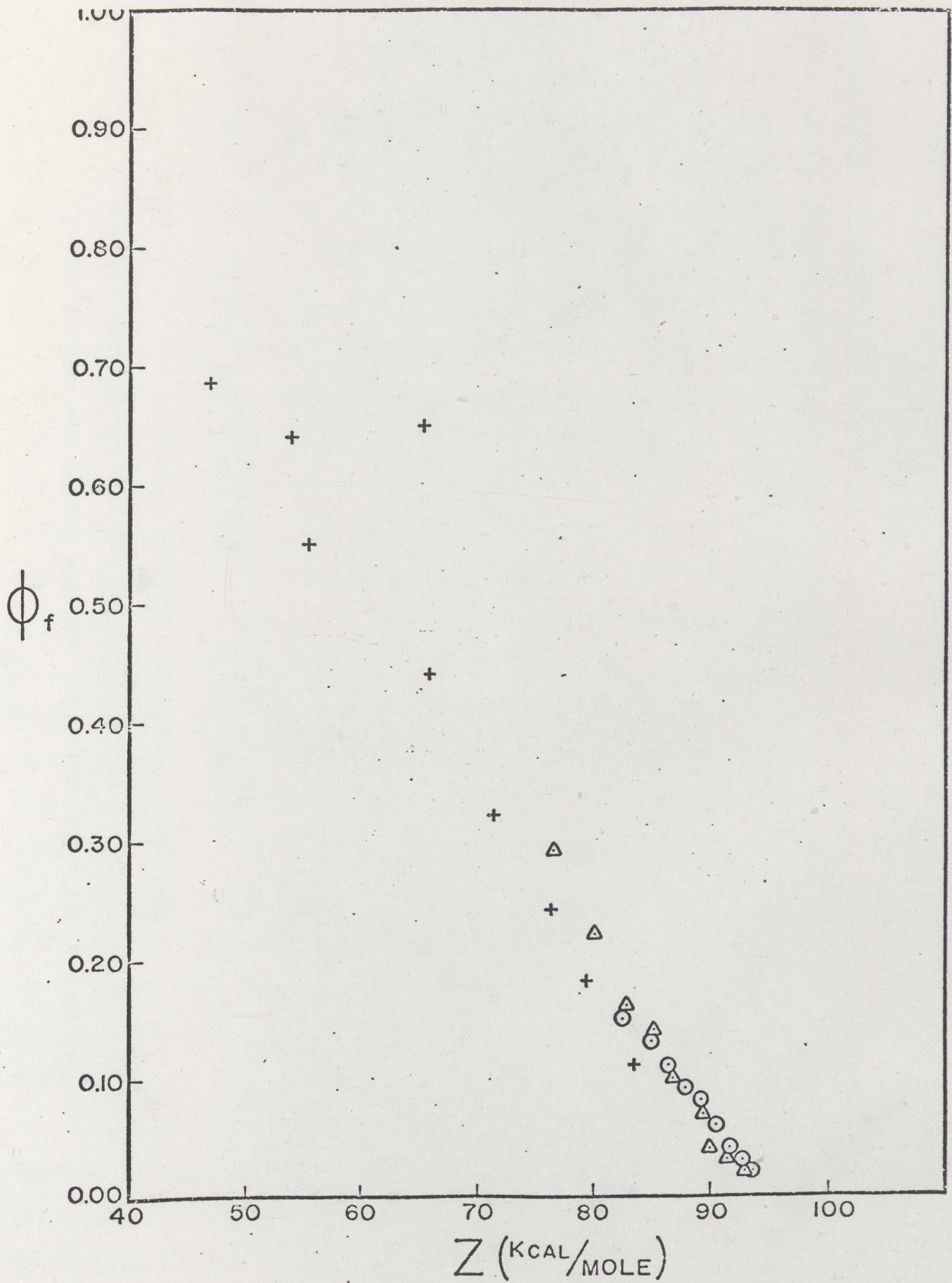
TABLE 2.

Values of the Radiative ($S_1 \rightarrow S_0$) and the Sum of the Radiationless

Rate Constants ($S_1 \leadsto T_1$, $S_1 \leadsto S_0$) and Estimated Singlet-Triplet (S_1-T_1)

Split for 9-COOCH$_3$ in Several Solvents

Solvent	ϕ_f	k_f(x10^{-7} sec^{-1})	$(k_{ix} + k_{ic})$(x10^{-7} sec^{-1})	$E(S_1-T_1)$[d]
Cyclohexane	0.68	5.2[a]	2.4[a]	7400 cm^{-1}
Benzonitrile	0.65	5.1[a]	2.7[a]	6700 cm^{-1}
Benzene	0.64	4.5[a]	2.5[a]	7000 cm^{-1}
Dioxane	0.55	3.8[a]	3.1[a]	7100 cm^{-1}
Acetone	0.44	3.4[a]	4.3[a]	6800 cm^{-1}
Acetonitrile	0.32	3.9[a]	8.4[a]	6600 cm^{-1}
Ethanol	0.18	4.4[b]	18.7[b]	6400 cm^{-1}
Methanol	0.11	6.5[c]	52.6[c]	6300 cm^{-1}
Dioxane (50%)	0.10	7.7[c]	69.3[c]	6100 cm^{-1}
Ethanol (50%)	0.08	4.2[c]	48.3[c]	5900 cm^{-1}

(a) $\pm$ 15%

(b) $\pm$ 25%

(c) $\pm$ 50%

(d) S_1 is fluorescence maximum, T_1 is assumed to be 14,700 cm^{-1} which is the T_1 energy for anthracene.

first three solvents, where $\phi_f > 0.60$, show no significant
change in either k_f or $(k_{ic} + k_{ix})$. In the second three
solvents, ϕ_f decreases from 0.55 to 0.32 with increasing
solvent polarity. The reason for this change in ϕ_f is that
the k_f values are decreasing and the values for $(k_{ic} + k_{ix})$
are increasing. However, the observed change in both sets of
rate constants in this category, relative to the first cate-
gory, is less than two fold, except for acetonitrile. The
final category contains the solvents where $\phi_f < 0.20$. The
rate constants given for these solvents are subject to greater
error because of the uncertainty in the very short fluorescence
lifetimes (τ_f). In spite of this fact, the trends in the two
sets of rate constants are clearly observable. The k_f values
in these solvents vary by less than a factor of two. Also it
should be noted that the k_f values for the protic solvents are
not markedly different than the k_f values for the aprotic
solvents. The $(k_{ic} + k_{ix})$ values, on the other hand, vary
greatly, and these values for the protic solvents are 2-25 times
greater than the $(k_{ic} + k_{ix})$ values for the aprotic solvents.
Thus, it is apparent that the increase in efficiency of the
non-radiative processes causes the greatly reduced ϕ_f in pro-
tic solvents.

The ratio of the intensities of 9-$COOCH_3$ fluorescence in
90% water - 10% dioxane and in 90% deuterium - 10% dioxane was
measured by comparing the areas under the fluorescence spectra
in the two solvents. In this manner the ϕ_f value was found to
be 14% greater in the latter solvent mixture.

Investigation of the fluorescence behavior of 9-COOCH$_3$ and of 9-tert-butyl anthroate dissolved in various mixtures of benzene and paraffin oil revealed three changes on increasing the percentage of paraffin oil in the solvent mixture. First, the ϕ_f values, as evidenced by the area under the curve, increased. This increase was ca. 40% for 9-COOCH$_3$ and ca. 29% for 9-tert-butyl anthroate in going from 100% benzene - 0% paraffin oil to 10% benzene - 90% paraffin oil. Second, there was slight structure present in the spectra of these two esters when the percentage of paraffin oil was greater than 60%. Third, the fluorescence maximum for 9-COOCH$_3$ did not shift, while for 9-tert-butyl anthroate, the fluorescence maximum blue shifted approximately 10 nm over the same range of solvent mixture.

The fluorescence spectra of 9-COOCH$_3$ and 9-tert-butyl anthroate in 100% paraffin oil followed the trends mentioned above for quantum yield and structure (Figures 5, 6). The 9-COOCH$_3$ fluorescence maximum, blue shifted approximately 20 nm from its position in 100% benzene. An estimate of the ϕ_f increase could not be made because the absorbance of these two solutions varied considerably from the others and from each other, and the spectra were uncorrected.

FIGURE 5.

The Fluorescence Spectrum of

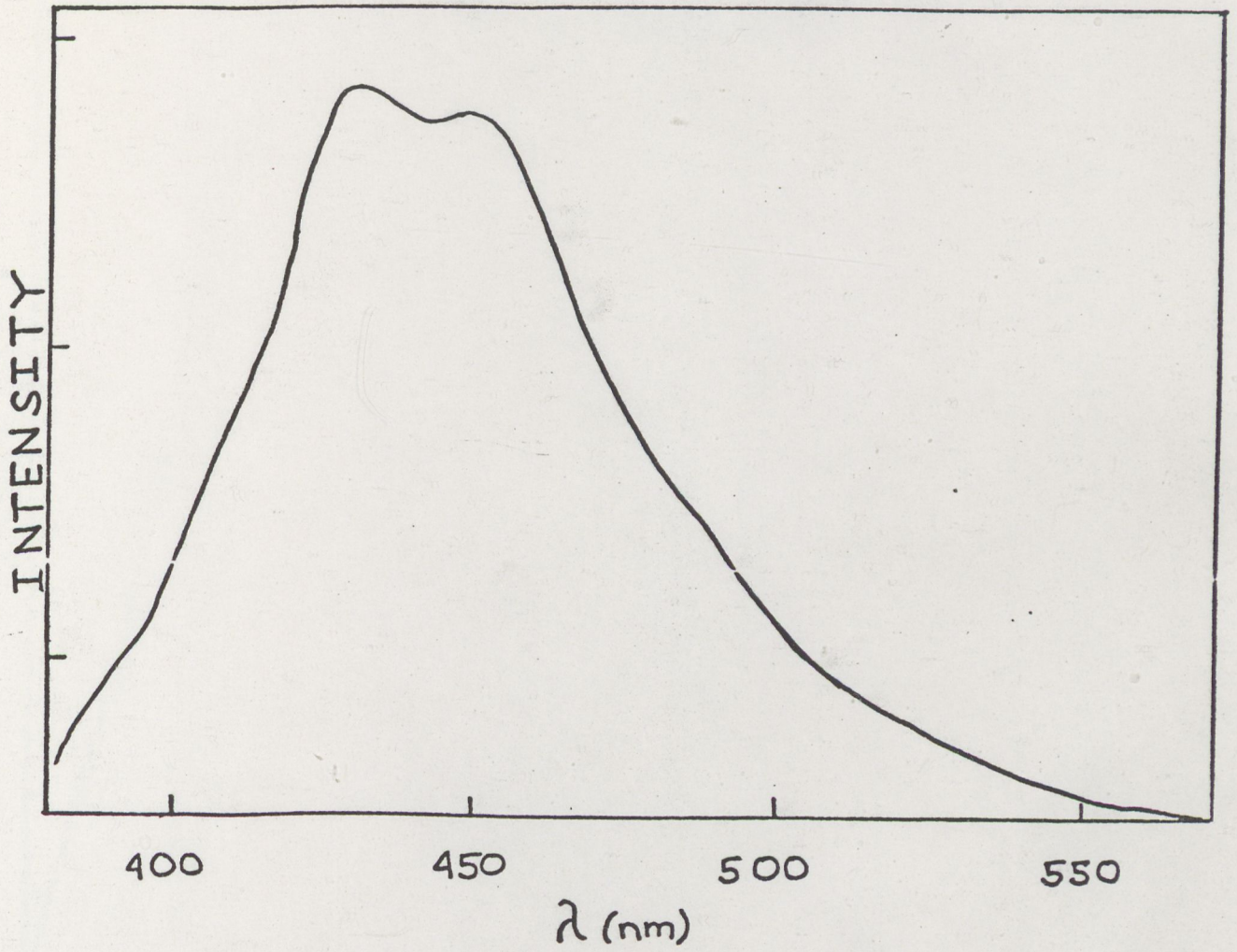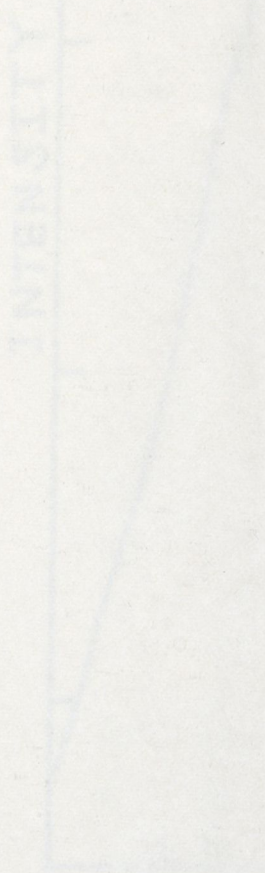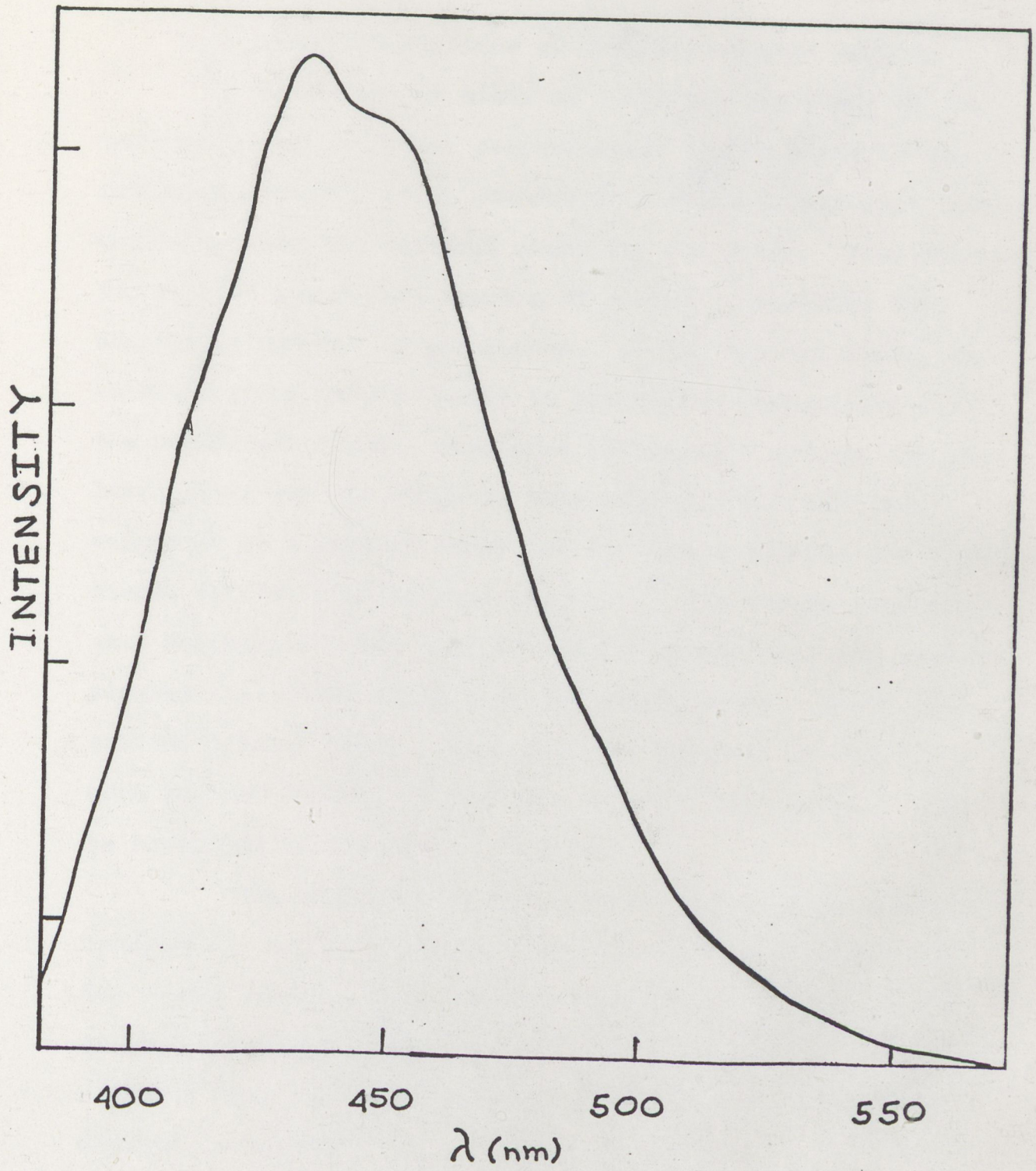9-COOCH$_3$ in 100% Paraffin Oil

(1.9 x 10^{-5} M, 1.00 cm cell)
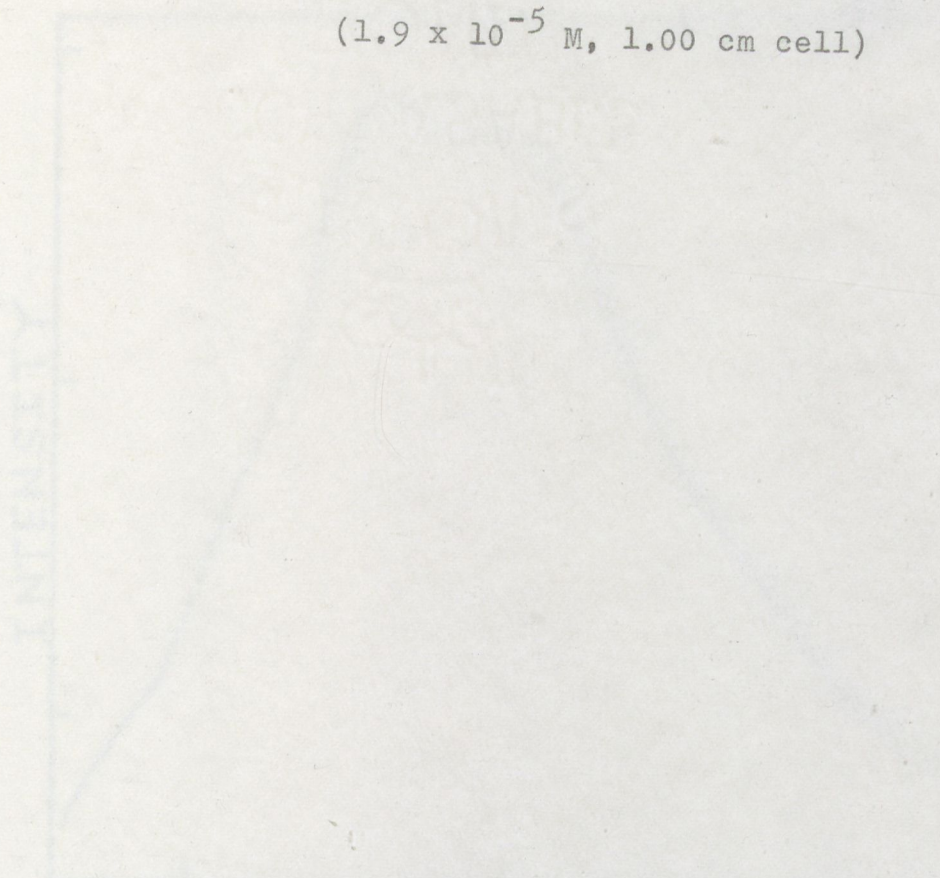
FIGURE 6.

The Fluorescence Spectrum of

9-tert-Butyl Anthroate in 100% Paraffin Oil

$(3.1 \times 10^{-5}$ M, 1.00 cm cell)

DISCUSSION

I.   Solvent Dependence of the Fluorescence Maximum

In the ground state of 9-COOCH_3, the plane of the carboxyl group is nearly perpendicular to the plane of the anthracene rings[2], which results in a minimal resonance inter-action between the carboxyl group and the rings. This accounts for why the absorption spectra of 9-COOCH_3 resembles the absorption spectra of anthracene. In the excited state, the carboxyl group rotates until it approaches coplanarity with the anthracene rings. Resonance interaction between the car-boxyl group and the rings in this configuration has been suggested as a partial cause for the broad, diffuse and highly Stokes shifted fluorescence spectrum.[1] The charge separation that accompanies this charge-transfer should make the excited singlet state more polar than the ground state. Hence, the excited singlet state energy would be expected to exhibit more solvent dependence than the ground state energy. This is confirmed by the plot in Figure 3.

The magnitude of the excited state charge transfer interaction can be evaluated from the solvent dependence of the Stokes shift. From previous theoretical treatments of solvent dependent fluorescence[11, 12, 13], Equation 4 is obtained when the solute-solvent interaction is primarily dipolar in nature.[14]

$$\tilde{\nu}_a - \tilde{\nu}_f \approx \frac{2}{hC_o}\left(\frac{\epsilon -1}{2\epsilon +1} - \frac{n^2-1}{2n^2+1}\right)\left(\frac{(\mu_e - \mu_g)^2}{a^3}\right) + \text{constant}$$

(4)

The terms are defined as follows: $\tilde{\nu}_a - \tilde{\nu}_f$ is the Stokes shift as defined previously (see Results), h is Plank's constant, C_0 is the speed of light in a vacuum, ϵ is the solvent dielectric constant, n is the solvent refractive index, μ_e is the dipole moment of the lowest excited singlet state of 9-COOCH_3, μ_g is the ground state dipole moment of 9-COOCH_3, and a is the Onsager cavity radius for 9-COOCH_3. The a value for 9-COOCH_3 is estimated to be $5\overset{\circ}{A}$. This value was estimated from X-ray diffraction studies of anthracene[15] and by using Fisher-Hershfeld-Taylor models of 9-COOCH_3.

Since a is known, $\mu_e - \mu_g$ can be determined from the slope of a plot of the Stokes shift versus the dielectric constant - refractive index term of Equation 4. This plot is shown in Figure 7 for 9-COOCH_3, in several solvents. The line is drawn through the circled points which represent data from polar aprotic solvents because it is these solvents whose interaction is primarily dipolar in nature. From the slope of this line, the $\mu_e - \mu_g$ value is determined to be 4.5 D. The accuracy of this number is critically dependent upon the Onsager cavity radius. However, even with a possible error of $\pm$ 50%, as previously estimated,[14] the $\mu_e - \mu_g$ is indicative of a rather polar excited state. By comparison, Mataga et al have found $\mu_e - \mu_g$ to be 0.5 - 1.0 D for β-naphthyl methyl ether and α, β-naphthols[11] while Seliskar and Brand found $\mu_e - \mu_g$ to be 9 D for 2-aminonaphthalene-6-sulfonate.[14]

FIGURE 7.

The Stokes Shift of 9-COOCH$_3$ Fluorescence as
a Function of Solvent Polarity Parameters

The numbers refer to the following solvents:

    1 - Ethyl Ether

    2 - Benzonitrile

    3 - Methyl Formate

    4 - N,N-Dimethyl-Formamide

    5 - Acetone

    6 - Acetonitrile

    7 - 80% Dioxane-20% Water

    8 - 60% Dioxane-40% Water

    9 - 40% Dioxane-60% Water

  10 - 20% Dioxane-80% Water

Y-axis: $(\nu_a - \nu_f) \times 10^{-3} cm^{-1}$

Values: 6.0, 5.6, 5.2, 4.8, 4.4, 4.0, 3.6

X-axis: $\dfrac{\epsilon-1}{2\epsilon+1} - \dfrac{n^2-1}{2n^2+1}$

Values: 0.15, 0.20, 0.25, 0.30

Data points: 1, 2, 3, 4, 5, 6, 7, 8, 9, 10
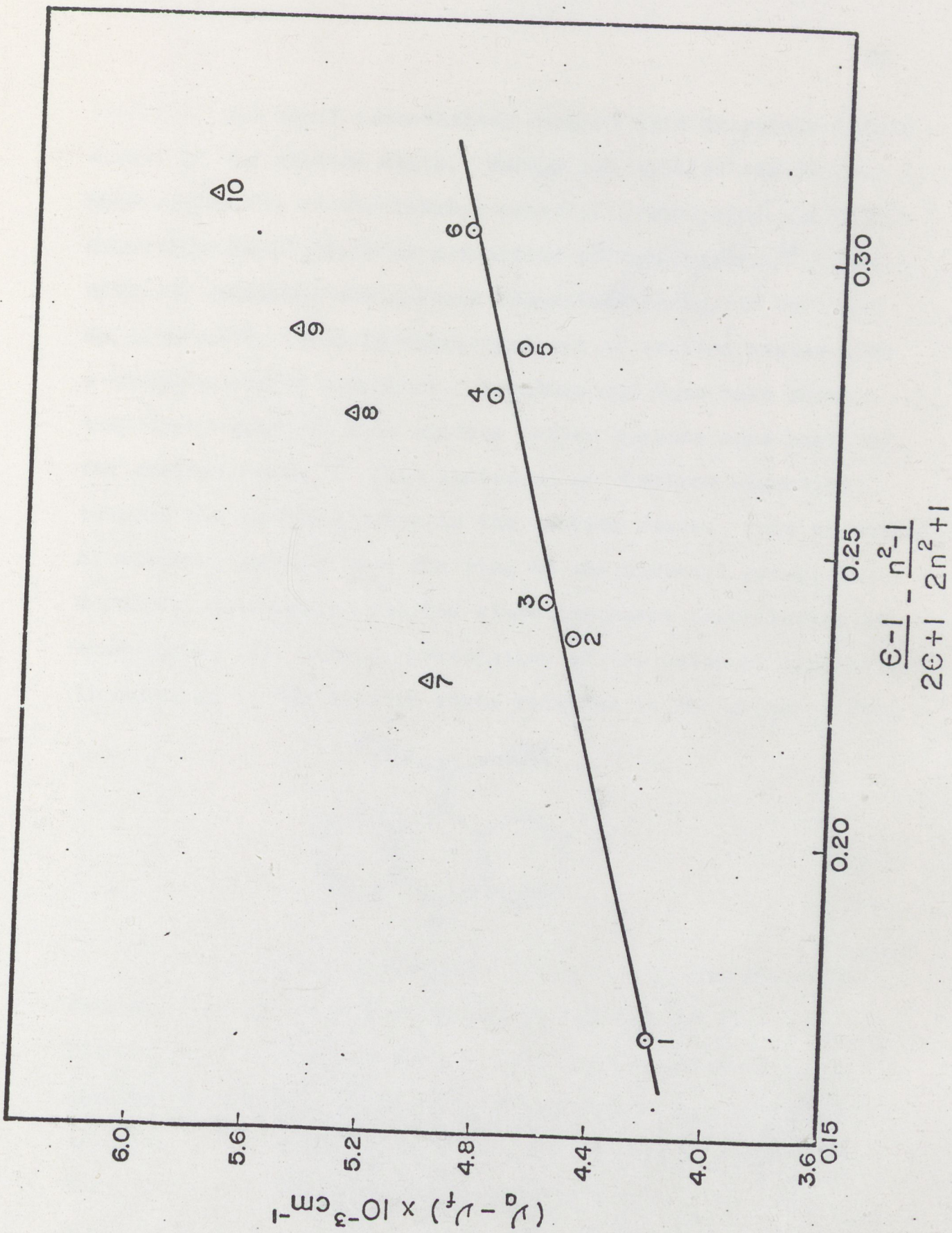
Two other observations support this increased dipole moment of the excited state. Werner has studied the fluorescence spectra of the t-butyl ester of 9-anthroic acid in ethanol/methanol (1:5) as a function of temperature.[16] From this, he estimates the solvent relaxation energy to be ca. 1500 cm^{-1}, which is characteristic of excited states with a charge-transfer component. Schulman and Pace have shown that the 9-anthroic acid acidium cation becomes more basic in the excited state.[17] This indicates an electron migration towards the carboxyl group in the excited state. This migration of electron density from the ring to the carboxyl group in 9-COOCH$_3$, produces an excited state resonance contribution as shown below (I). Hence, protonation of the carboxyl type oxygen is enhanced in the excited state relative to the ground state.
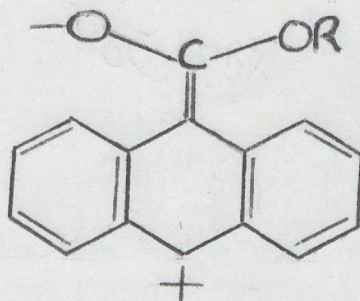
(I)

The points (triangular shaped) that significantly deviate from the line through polar, aprotic solvents in Figure 7 are from data taken in dioxane-water mixtures. Similar deviations are observed for all data taken from protic solvents. This means that the Stokes shift is greater than that predicted from only dipole-dipole interaction. This additional Stokes shift is believed to be due to the hydrogen

bond contribution to the excited state solvation which, from Figure 7, can be seen to be a fairly large contribution. Referring again to structure I, it is apparent that a stronger hydrogen bond would be formed between the solvent and the coplanar excited state than between the solvent and nearly perpendicular ground state.

II.   Solvent Dependence of $\emptyset_f$

A large increase in $\emptyset_f$ for 9-COOCH$_3$ in the non-polar and some of the polar aprotic solvents is an anomaly. In general, meta directing substituents, like a carboxyl group, tend to inhibit the fluorescence of the parent hydrocarbon.[3]

One possible explanation for this enhancement of the $\emptyset_f$ for 9-COOCH$_3$ may be due to the relative energies in the singlet and triplet manifolds. The first (T_1) and second (T_2) triplet levels are located at 14,700 cm^{-1} and 26,050 cm^{-1} respectively for anthracene.[10] The lowest excited singlet level (S_1) is only 650 cm^{-1} above T_2, so that favorable Franck-Condon factors permit the intersystem crossing process ($S_1 \rightsquigarrow T_2$) to compete quite well with fluorescence.[10] Internal conversion ($S_1 \rightsquigarrow S_0$) is known to be negligible for anthracene.[10]

The situation may be different for 9-COOCH$_3$. Attempts to locate the triplet levels by phosphorescence and triplet-triplet absorption have been unsuccessful.[18] It is known, however, that triplet states are generally less affected by charge-transfer effects than singlet states. Therefore, it

is expected that the shift in the energies of T_1 and T_2 for 9-$COOCH_3$ relative to those of anthracene would be much smaller than the shift in S_1. From the fluorescence maxima data (see Table 1.), S_1 of 9-$COOCH_3$ is ca. 3000 cm^{-1} lower in energy than the S_1 level of anthracene. If it is assumed that the energy shift of T_1 and T_2 are considerably less than this, S_1 could now be as low as 2000 cm^{-1} below T_2. Franck-Condon factors would now prohibit the crossing to T_2 from S_1. In fact to do this would require a substantial activation energy. Even though S_1 has shifted considerably, it would still remain far enough above T_1 so that $S_1 \rightsquigarrow T_1$ would still be inefficient due to unfavorable Franck-Condon factors. Hence, intersystem crossing for 9-$COOCH_3$ might compete less effectively with fluorescence than it does in the anthracene molecule. This would result in the observed increase in $\emptyset_f$ of 9-$COOCH_3$ relative to the $\emptyset_f$ of anthracene. Cowen and Schmiegel have suggested a similar ordering of the electronic energy levels for 9-anthroic acid.[19]

It is also possible that the intersystem crossing rate might be affected by geometry differences between S_1 and the triplet states. Since charge-transfer effects are smaller in T_1 and T_2 than in S_1, it is possible that the triplet levels and the ground state have the same geometry. This could lead to unusually small vibrational overlap factors which control the radiationless transition $S \rightsquigarrow T$ even if the energy of S_1 is closer to that of T_1 or T_2 than anticipated above. Lim et al[20] have suggested the existance of such "geometry factors".

From Table 2, the Z dependent solvent quenching of $9\text{-}COOCH_3$ fluorescence is seen to be greatest in solvent or solvent mixtures which have hydrogen bond donor capabilities. The increase in the non-radiative decay rates in these protic solvents is the primary reason for this quenching. Also, it should be noted that the magnitude of $(k_{ix} + k_{ic})$ is greater for methanol and the water containing solvents than for ethanol. This is in complete agreement with the relative hydrogen bond donor abilities of these solvents.

Due to the lack of information on the $9\text{-}COOCH_3$ triplet, the relative contributions of k_{ix} and k_{ic} to the quenching process cannot be determined. It is possible, though, to make some comment on possible quenching pathways. Over the range of solvents used, the fluorescence maxima shift is ca. 2000 cm^{-1} (see Table 1). If the shift in T_1 is assumed to be considerably less, $\Delta E(S_1 - T_1)$ should decrease with increasing solvent polarity. Seliskar and Brand have shown that such a situation led to fluorescence quenching by enhancing the rate of intersystem crossing $(S_1 \rightsquigarrow T_1)$ for aminolonaphthalene-6sulfonate derivatives.[14] A list of estimates of $\Delta E(S_1 - T_1)$ for $9\text{-}COOCH_3$ as given in Table 2. To make these estimates it was assumed that T_1 has the same energy as it does in anthracene ($14,700 \text{ cm}^{-1}$). The $\Delta E(S_1 - T_1)$ does decrease in the protic solvent as the $\emptyset_f$ decreases, but the decrease is not that marked. The minimum value of $\Delta E(S_1 - T_1)$ is still far too large to produce significant Franck-Condon integrals between S_1 and T_1. Also, the

difference between the $\Delta E(S_1 - T_1)$ values in protic and in
aprotic solvents is not large enough to explain the vast
differences in ϕ_f between these two groups of solvents. If
this mechanism were to be operative for 9-COOCH$_3$, there would
have to be a triplet level at ca. 20,000 cm^{-1}. This would
mean that either T_1 shifts to a higher energy by ca. 6000 cm^{-1}
or T_2 shifts to a lower energy by ca. 6000 cm^{-1} relative to
their respective locations in anthracene. Either case is
unlikely and thus an enhanced k_{ix} by this procedure is improb-
able.

Since enhancement of k_{ix} is seen to be improbable
by this mechanism, and there is strong solvent induced quenching
observed in protic solvents due to hydrogen bond interaction
between structure I and the solvent, it is believed that k_{ic}
is more solvent dependent than k_{ix} and is responsible for the
decrease in ϕ_f in these solvents. The importance of the hydro-
gen bond interaction is demonstrated by a 14% increase in ϕ_f
when 9-COOCH$_3$ is dissolved in 90% D$_2$O - 10% dioxane relative
to a 90% H$_2$O - 10% dioxane solution of this same ester. This
strong interaction may provide a coupling between the excited
state solute and solvent and the result being an enhancement
of the internal conversion rate with subsequent loss of exci-
tation energy to the vibrational modes of the environment. A
deuterium effect on N,N-dimethyl-1-amino-5-naphthalene sulfonate
fluorescence has been previously accounted for by such a

mechanism.[21] In addition, enhanced internal conversion rates could account for the failure to observe the 9-COOCH$_3$ triplet by flash or phosphorescence in protic solvents.[18]

A decreasing radiative rate constant also contributes to the observed quenching in aprotic solvents (Table 2). The dependence of the k_f on the square of the refractive index of the solvent is the reason for this variation in k_f.[22] The observed variation in ($k_{ix} + k_{ic}$) for these solvents is again most likely due to an enhanced k_{ic} resulting from the greater solute-solvent interaction as solvent polarity increases.

It should be pointed out that the benzonitrile data represents an exception of the $\emptyset_f$ dependence of solvent polarity. Based on Z values, the $\emptyset_f$ of benzonitrile should be closer to the $\emptyset_f$ of acetone. Apparently the coupling between benzonitrile and excited 9-COOCH$_3$ which leads to increased k_{ic} values is smaller than solvent polarity would reflect.

III.   Viscosity Dependence of $\emptyset_f$

Mixtures of benzene and paraffin oil were used as viscous solvents in an attempt to block the carboxyl group rotation in two esters of 9-anthroic acid. The refractive indices of these mixtures are known to be constant.[23] The spectral changes observed for both esters, however, followed the same trends set by 9-COOCH$_3$ when it is placed in increasingly non-polar solvents. That is, as the solvent polarity decreased, the $\emptyset_f$ increased, the fluorescence maximum blue shifted, and

slight structure appeared in the spectra. The spectral data taken from the solvent mixtures containing the higher percentage of paraffin oil closely resembled the spectrum obtained when cyclohexane was the solvent for $9\text{-}COOCH_3$.

These results can be attributed to the solvent polarity and not viscosity effects. Benzene and paraffin oil are both non-polar solvents. However, the benzene has a cloud of delocalized electrons which the paraffin oil does not. This makes the benzene much more easily polarized than the paraffin oil which, in a sense, makes the benzene more "polar". In the polar aprotic and non-polar solvents used in the previous experiments, the solute-solvent interaction is believed to be dipole-dipole in nature. In the present case, the dipole change in the solute could possibly induce a dipole in the benzene due to the existence of the π cloud of delocalized electrons. Thus the system of solute and benzene has a dipole-induced dipole interaction. As the amount of benzene in the solvent mixture decreases, this dipole-induced dipole interaction decreases, and the solvent becomes less "polar".

SUGGESTIONS FOR FURTHER STUDY

This work has indicated that intermolecular hydrogen bonding may be responsible for the observed solvent quenching in increasingly polar solvents. The next step would be to investigate the affects of intramolecular hydrogen bonding. This can be done by using a molecule like 9-(2-hydroxyethanol)-anthroate (structure II) dissolved in a non-polar solvent.

$$O=\overset{\displaystyle |}{C}-O-CH_2-CH_2-OH$$
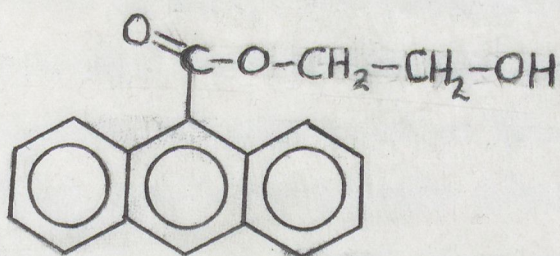
(II)

Changing the hydrocarbon chain of the esters of 9-anthroic acid will not change the absorption spectrum due to the position of the carboxyl group in the ground state. Therefore, the $\emptyset_f$ and Stokes shift for 9-(2-hydroxyethanol)-anthroate dissolved in cyclohexane, for example, can be compared to the spectral data of $9-COOCH_3$ and any differences will be due to differences in the excited state only. This data would give further evidence towards proving or disproving the affect of hydrogen bonding on solvent induced fluorescence quenching.

Another area that should be investigated is the triplet energy levels of $9-COOCH_3$. Since earlier attempts to locate the triplet state of this molecule have failed (see Discussion), it may be of value to attempt a Lamola-Hammond or Parker-Joyce

triplet-triplet energy transfer experiment. The results of
the experiment, if successful, would give data concerning the
relative contributions of k_{ix} and k_{ic} to the solvent induced
quenching of the 9-$COOCH_3$ fluorescence. This would support
or disprove the assumption made about the energy level of
the triplet state and make the conclusions to this work more
firm.

APPENDIX I

Sensitivity Calibration

The following procedure was followed to determine the
multiplication factors for the sample sensitivity settings
of the Perkin-Elmer-Hitachi-MPF-2A Spectrofluorometer. The
standard solution for this method was a solution of 9-methyl
anthroate dissolved in ethanol. The absorbance of this
solution at the wavelength maximum (362 nm) was 0.019.

An emission spectrum of this standard solution was taken
at each of the various sample sensitivity settings (1-5). In
order to keep the spectra on the chart paper and at the same
time get a measurable spectrum, the slit widths on the emission
monochromater were adjusted so that spectra taken on two consec-
utive sample sensitivity settings were on scale. All other
conditions were held constant. Hence, for any two consecutive
sample sensitivity settings, there were emission spectra
taken at exactly the same conditions. For instance, sample
sensitivity settings 4 and 5 had emission spectra taken with
the emission monochromater slit width set at 1.5 nm, while
sample sensitivity settings 3 and 4 had the slit width set
at 3.0 nm. This process was continued for sample sensitivity
settings 2 and 3 and 1 and 2. There were eight emission spec-
tra (4 sets of 2) taken in all.

All of the emission spectra were of the same standard
solution, therefore, the only difference in one set of
emission spectra was the area under the spectra. Since the
area is directly proportional to the weight of the chart
paper, the ratio of the weights were obtained for each set of
spectra. This ratio of the weight of the spectrum at the
higher sample sensitivity setting to the weight of the spec-
trum at the lower setting was used to determine the multipli-
cation factor needed to convert from one sample sensitivity
setting to the next.

Example: Spectrum S-1

Excitation Monochromater	362 nm
Slit Width	7 nm
Emission Slit Width	1.5 nm
Reference Sensitivity	2
Sample Sensitivity	5
Weight	0.7341 gm

Spectrum S-2

Excitation Monochromater	362 nm
Slit Width	7 nm
Emission Slit Width	1.5 nm
Reference Sensitivity	2
Sample Sensitivity	4
Weight	0.2218 gm

$$\frac{\text{Weight S-1}}{\text{Weight S-2}} = \frac{0.7341 \text{ gm}}{0.2218 \text{ gm}} = 3.3$$

In going from sample sensitivity 4 to sample sensitivity 5, multiply by 3.3.

See Table 3 for a complete list of sample sensitivity multiplication factors.

TABLE 3.

Sensitivity Scale of Perkin-Elmer-

Hitachi-MPF-2A Spectrofluorometer

(Based on sample sensitivity 1 as 1.00)

Sample Sensitivity Setting	Sensitivity Factor	
1	x 1.00	
		(3.0)
2	x 3.0	
		(3.4)
3	x 10.2	
		(2.8)
4	x 28.6	
		(3.3)
5	x 94.6	

APPENDIX II

Computer Program to Correct Fluorescence

Emission Spectra

See Table 4 for the actual computer program.

I.   Setting Up the Data Cards

Sensitivity - symbol S(I)

There is a sensitivity data point for every
two nanometers from 380 - 580 nm. The
sensitivity, S, for 380 nm is put in the
array as S(1), the sensitivity at 382 nm
is put in the array at S(3), etc..

Number of sets of data - symbol N

The number of sets of data to be processed
at one time should be punched on the card
so that the last digit of the number is in
card column three. This must be a whole
number with no decimal points.

Number of data points in a particular set -
symbol M

This number should also be punched on
card so that the last digit of the number
is in card column three. It must also be
a whole number with no decimal point.

Raw data - symbol RD

    The wavelength is referred to as LAMBDA.
Each data point is printed on its own
data card in the following manner.

    The wavelength is printed in the first
ten spaces of the card, followed by a
decimal point. The raw data is printed
on the card beginning with card column
eleven. It must also have a decimal
point in it.

    Example:

λ (in nm)										raw data (in cm)				
3	8	4	.							1	5	.	6	

cc→

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |

    Note: Use only even wavelengths, i.e., 380,
382, 384, etc.

    The data cards should be set up in this
order; N, M_1, (first set of raw data),
M_2, (second set of raw data), etc.

II.   What the Program Does

Line 1 makes LAMBDA a real variable instead
of its normal integer meaning. LAMBDA
will be used for the wavelength of the
data.

Line 2 dimensionalizes the variable S, which
will be used to store the sensitivity
curve.

Lines 3 and 4 read the sensitivity curve into
the computer with a value given for every
two nanometers. The value at 380 nm is
at address S(1), the value at 382 nm is
at address S(3), etc. There are eight
data prints (sensitivity curve) per card.

Lines 5 and 6 read in N, the number of different
sets of data that will be corrected at
one time.

Line 7 sets up a loop to go through each set
of data and correct them separately.

Lines 8 and 9 print out column headings for
the results.

Line 10 sets the area under the curve, symbolized
by AREA, equal to zero (0.0)

Lines 11 and 12 read M, the number of data prints
in one set of data.

Line 13 sets up a loop that does the actual
arithmetic that corrects each data point.

Lines 14 and 15 read in the wavelength (LAMBDA)
and the raw data (RD) from the data card.

Line 16 sets J, an index number, to a number
that will make the wavelengths of the raw
data coincide with the index number of S.

S(1) is for 380 nm

J = 380 nm-379 nm = 1 is for 380 nm

Lines 18 and 19 print out the wavelength (LAMBDA),
the raw data (RD) and the corrected data (Z)
under the column headings printed in
Lines 8 and 9.

Line 20 adds the area of that point to the
existing area. The actual areas under
the curve are not being calculated. To
do this, one must multiply by the width
of the integral. For this line to work,
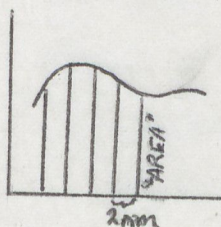
"AREA" x 2 nm = true
area of that part. To
get the total area,
add up all these parts.

every 2 nm must have a data point. The
width of the integral would then be 2 nm.
Since one is only interested in the ratio of
areas, one can neglect multiplying by the
width because it would just cancel out.

Lines 21 and 22 print out the words "Area

Under the Curve Is:" and then the numerical

area.

Line 23 is a CONTINUE statement that tells the

computer to go to line 13 and do lines 13

through 23 until M is reached. Once M is

reached, this line tells the computer to

go to line 7 and perform lines 8 through

23 until N is reached.

TABLE 4.

Correcting Raw Spectral Data [a]

Line Number[b]	Statement Number	Statement
1		REAL LAMBDA
2		DIMENSION S(220)
3		READ (50,2) (S(I), I = 1, 202, 2)
4	2	FORMAT (8 F 10.0)
5		READ (50, 4) N
6	4	FORMAT (I3)
7		DO 65 K = 1, N
8		WRITE (66, 1)
9	1	FORMAT (5X, "LAMBDA", 5X, "RAW DATA", 5X, "CORRECTED DATA", //)
10		AREA = 0.0
11		READ (50, 6) M
12	6	FORMAT (I3)
13		DO 11 L = 1, M
14		READ (50, 3) LAMBDA, RD
15	3	FORMAT (2 F 10.0)
16		J = LAMBDA - 379
17		Z = RD/S(J)
18		WRITE (66, 20) LAMBDA, RD, Z
19	20	FORMAT (6X, F 5.0, 5X, F 6.2, 9X, F 6.2, /)
20	11	AREA = AREA + Z

TABLE 4. (cont'd)

Line Number (b)	Statement Number	Statement
21		WRITE (66, 30) AREA
22	30	FORMAT (5X, "AREA UNDER THE CURVE IS:", 5X, F 10.2, ////)
23	65	CONTINUE
24	100	STOP
25		END

(a) This program is written in Fast Fortran Computer Language. It can be used for Fortram Language with slight modifications.

(b) These numbers are not used when using this program. They are inserted in this table for identification purposes.

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