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SOLVENT STARK EFFECTS AND SPECTRAL SHIFTS. II.*

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ABSTRACT

Solvent shifts of the energies of the lowest ^1L_a bands of the electronic
absorption spectra of anthracene, chrysene, phenanthrene, and tetracene and
of the lowest ^1L_b bands of the electronic absorption spectra of naphthalene,
phenanthrene, chrysene, and picene are reported. The origins of these shifts
are analyzed in terms of theories developed by Baur and Nicol and by Abe.
Satisfactory fits of the experimental data are obtained for theoretical
expressions derived from both theories, but discrepancies are observed
between the relative magnitudes assigned to the various contributions to
the shifts by the two theories. The magnitudes of the parameters of the
Baur and Nicol theory, relating solvent shifts to the dielectric constant
and refractive index of the solvent, are found to be the same within
experimental precision for the ^1L_a transitions in all of the molecules
studied; a similar regularity of the parameters for the ^1L_b transitions
also is observed.

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I. INTRODUCTION

Paper I[1] in this series reported on a theoretical analysis of the effects of polar solvents on the energies of electronic absorption spectra of nonpolar solutes. The second-order perturbation theory treatment of these effects by McRae[2] identified two contributions which arise from (1) polarization of the solute by the permanent dipole moments of the solvent and (2) the mutual induced-polarization of the solute and solvent. These contributions were analyzed in I in terms of a dielectric continuum model of the solution in order to determine the functional dependence of these solvent spectral effects (especially contribution (1)) on the macroscopic dielectric properties of the solvent.

The solvent dependence of contribution (2) was taken from the work of McRae to have the form:

$$\Delta v_2 = A \frac{(n^2 - 1)}{(2n^2 + 1)} \tag{1}$$

Δv is the shift of the transition frequency from that (herein designated v_o) of the isolated, non-interacting solute to that for the solute in a medium of refractive index n. v_o is typically taken to be identical with the transition frequency for the solute in the vapor phase, but here it is treated as an adjustable parameter to be compared with the vapor phase transition frequency. In the present treatment, A is taken to be a solute- and transition-dependent parameter which is assumed to be solvent-independent, although McRae has demonstrated that the magnitude of A should depend on an averaged energy of the absorption spectrum of the solvent.[2]

Contribution (1) to the solvent spectral shift was analyzed in I by using a fluctuation approach similar to one given by Fröhlich.[3] The solute in a particular electronic state was represented by a spherical volume of radius d and electric polarizability α imbedded in a continuum of dielectric

constant ϵ and refractive index n. The average energy of interaction between the solute and the solvent was expressed as $\alpha \langle E^2 \rangle_{Av}$, where $\langle E^2 \rangle_{Av}$ is the mean square of the fluctuating electric field at the site of the solute molecule due to the polarization of the permanent solvent dipoles. In order to evaluate $\langle E^2 \rangle_{Av}$, it was necessary to divide the solvent into two regions such that $\langle E^2 \rangle_{Av}$ could be assigned completely to molecules contained within a spherical shell of radius R, centrosymmetric with the solute molecule. Details of this model and its development are given in I.

This model yields for $\langle E^2 \rangle_{Av}$ the expression:

$$\langle E^2 \rangle_{Av} = \frac{36 \ln^2(R/d)}{3R^3} \left[kT \frac{(\epsilon-1)(2\epsilon+1)}{\epsilon} \right] \qquad (2)$$

Here, k is the Boltzman constant; and T is the absolute temperature of the solution. By using this expression, contribution (1) to the solvent shift is predicted to be:

$$\Delta v_1 = \left[\frac{36kT(\alpha_e - \alpha_g)}{R^3} \ln^2 \left(\frac{R}{d} \right) \right] \left[\frac{(\epsilon-1)(2\epsilon+1)}{3\epsilon} \right] \qquad (3)$$

In eq. 3, α_g and α_e are the electric polarizabilities of the solute in the ground and appropriate excited electronic states respectively.

It was argued in I that the term within the first brackets on the right hand side of eq. 3 is approximately independent of solvent, which was represented in I by setting it equal to a constant 3B. The total shift Δv of the transition frequency from that in the unperturbed molecule is the sum of Δv_1 and Δv_2.

$$\Delta v = \Delta v_1 + \Delta v_2 = A \frac{(n^2-1)}{(2n^2+1)} + B \frac{(\epsilon-1)(2\epsilon+1)}{\epsilon} \qquad (4)$$

Abe[4] has pointed out that, in addition to the contribution due to the permanent dipoles of the solvent, eq. 2 for $\langle E^2 \rangle_{Av}$ includes a contribution of the induced polarization of the solvent. A correction removing this can be made[4,5] by multiplying eq. 2 by the factor:

$$\left(\frac{3}{n^2+2}\right)\left(\frac{\epsilon-n^2}{\epsilon-1}\right)\left(\frac{2\epsilon+n^2}{2\epsilon+1}\right) \tag{5}$$

This yields for contribution (1):

$$\Delta\nu_2 = \left[\frac{36kT(\alpha_e-\alpha_g)}{R^3}\ln^2\left(\frac{R}{d}\right)\right]\left[\frac{(\epsilon-n^2)(2\epsilon+n^2)}{(n^2+2)\ \epsilon}\right] \tag{6}$$

$$= B\left[\frac{(\epsilon-n^2)(2\epsilon+n^2)}{(n^2+2)\ \epsilon}\right]$$

In eq. 6, B is treated as a solvent independent parameter which is approximately three times the magnitude of the factor B used in I and in eq. 4. By combining eqs. 1 and 6, the following expression is obtained for the spectral solvent shift which will be used in this paper.

$$\Delta\nu = \nu_i - \nu_o = A\frac{(n^2-1)}{(2n^2+1)} + B\frac{(\epsilon-n^2)(2\epsilon+n^2)}{(n^2+2)\ \epsilon} \tag{7}$$

In eq. 7, ν_i is the transition frequency in a solvent of dielectric constant ϵ and refractive index n.

A correlation of polar solvent shift data for the ^1L_a band of tetracene, taken by Weigang and Wild,[6] with the predictions of this theory also was reported in I. This investigation of polar solvent shifts has been extended to examine shifts of parts of the absorption spectra of other aromatic molecules, including the ^1L_a transitions of anthracene, phenanthrene, and chrysene and ^1L_b transitions in chrysene, phenanthrene, picene, and naphthalene. The goals of this investigation were 1) to establish that the prediction represented by eq. 7 would correlate polar solvent shifts of other spectra and 2) to determine the solute dependence of the parameters

A and B for a particular type of electronic transition in a series of similar molecules.

II. EXPERIMENTAL

Except for the tetracene data taken from reference 6, all of the spectral data reported here were obtained with a Cary 14 recording spectrometer operated at room temperature (about 20°C). The instrumental calibration is known to be accurate to better than ± 2Å (integral) over the spectral range of interest. The reproducibility of the measurements reported here when different samples of the same solute-solvent pair were measured was typically ± 1 A.

Eastman H480 anthracene, Fisher zone-refined naphthalene, Eastman 4217 chrysene, and Aldrich 4200 picene were used without further purification. A highly purified grade of phenanthrene was obtained from Mr. Ed Yee of this department for this investigation. No impurities were detected in' the material by absorption spectroscopy, although a small concentration of impurities (probably anthracene) could be detected by delayed fluorescence. The best commercially available grades of the various solvents were used without further treatment. A list of these solvents is given in Table I.

III. ANALYSIS OF THE DATA

Transition frequencies v_i calculated from the wavelengths of the absorption band maxima of the various vibrational components, together with published values of the dielectric constants ϵ_i and refractive indices n_i of the various solvents were fitted to eq. 7 by a least squares procedure

$$v_i = v_o + A \frac{(n_i^2 - 1)}{(2n_i^2 + 1)} + B \frac{(\epsilon_i - n_i^2)(2\epsilon_i + n_i^2)}{(n_i^2 + 2)\,\epsilon_i} \qquad (7)$$

procedure described by Davies[7] to determine the best values and standard

deviations of the parameters ν_o, A, and B. This computation was made by using the IBM 7094 computer at the UCLA Computing Center. Dielectric constants appropriate to room temperature were taken from the U.S. National Bureau of Standards Table of Dielectric Constants of Pure Liquids (Circular No. 514), and refractive indices were obtained from the CRC Handbook of Chemistry and Physics and the Phillips Petroleum Reference Data for Hydrocarbons. The corresponding values of the functions $\left(n^2-1/2n^2+1\right)$ and $\dfrac{(\epsilon-n^2)(2\epsilon+n^2)}{(n^2+2)\ \epsilon}$ are listed in Table I.

This reduction technique, in which data from all of the solvents are treated simultaneously, differs from that used in analyzing the tetracene solvent shifts in I, where ν_o and A were determined graphically only with data for nonpolar hydrocarbon solvents. However, the values given by both techniques agree within the computed standard deviations of these parameters. Use of eq. 7 also changes the magnitude of B by approximately a factor of four from that obtained by using eq. 4; but it does not yield a significant improvement in the fit to the experimental data.

IV. RESULTS

1. Tetracene

In order that it may easily be compared with the new results reported for other solutes, the correlation of Weigang and Wild's data on the ^1L_a transition in tetracene by eq. 7 is reviewed briefly. By a plot of the frequency for the 0-0 band of the ^1L_a transition of tetracene versus the function $(n^2-1)/(2n^2+1)$, Fig. 1 shows how these data are correlated when only contribution (2) (eq. 1) is considered. The lines in Fig. 1 represent least squares fits to eq. 1 of the data for the hydrocarbons _____, haloalkanes __ _ ___ _ ___, alcohols __ __ __, and ketones _ _ _ _.

Although a relatively good fit is obtained within each class of solvents

except the alcohols, the calculated values of A differ by a factor of two; and there is a wide variation in the values of ν_o obtained by extrapolation of the refractive index to unity.

The improvement obtained when the data are correlated by eq. 7 can be seen in Fig. 2. Here, the experimental transition frequencies are plotted versus the frequency shifts calculated with the best-fit parameters that are listed in Table II. The solid line represents the computed best fit.

Three aspects of the fit obtained deserve attention:

1. The success of the correlation is reflected by the fact that the transition frequencies for all of the solvents are within 50 cm^{-1} of the best fit curve with the exceptions of dioxane (15) and t-butyl alcohol (11, which melts just at room temperature).

2. The data for all of the classes of solvents distinguished in Fig. 1 fall along lines essentially parallel to the best fit line.

3. However, two classes of solvents still can be distinguished. One class consists of the alcohols and hydrocarbons which group together above the line. The other consists of the ketones and some other solvents, many of which contain unsaturated bonds to heteroatoms, which are displaced about 50 to 80 cm^{-1} to lower energies. It is not yet clear to which, if either, of these classes the halogenated hydrocarbons belong.

This distinction between solvent classes also is observed to varying degrees in the data for the other solutes. It is beyond the purvue of the model used to develop the present theory to speculate in detail on the origins of this distinction. This might be attributed to the solvent dependence of the A parameter, the inadequacy of the approximation (described in I) that the magnitude of the ratio R/d is independent of solvent, or the crudeness of the continuum model.

2. Anthracene

The locations of the band maxima for as many as four vibrational components of the ^1L_a transition of anthracene were determined in as many as 46 solvents. These solvents included many of those used by Weigang and Wild and others, especially some polar aromatic solvents.[8] The correlation obtained with eq. 7 for the shifts of the 0-0 vibrational component of this band is represented in Fig. 3 by a plot of the data corresponding to that plotted for tetracene in Fig. 2. The correlations obtained for the three other components are equally good. (A complete list of transition frequencies for the various solute-solvent pairs is given in the Appendix.) The values of the parameters obtained from the least squares fits for these four vibrational components are listed in Table I.

Three things should be noted about these results:

1. The locations of all of the data points except those of cyclohexane (45), carbon tetrachloride (46), chloroform (47), acetaldehyde (48), and n-butyraldehyde (50) are within 50 cm^{-1} of the best fit curve. These five deviate by less than 80 cm^{-1}.

2. The values of the A and B parameters obtained for the different vibrational components of this band agree within experimental error. This is expected as the shift is primarily an electronic rather than a vibrational effect.

3. Also within the precision of the experiment, the relative ordering of the various solvents and magnitudes of the parameters A and B obtained for the ^1L_a band of anthracene are the same as those obtained for the ^1L_a band of tetracene. This result cannot be predicted by the theory of solvent shifts alone, although the similarity of solvents effects on these transitions in particular solvents has been observed.[9] The two classes of solvents observed for tetracene also can be distinguished here.

The similarity between the values of the parameters A and B obtained

for these two solutes lead us to examine whether the same constants would be
obtained for ^1L_a transitions in similar molecules. Pentacene, the next
higher homologue in this series of linear, catacondensed aromatic hydro-
carbons, is being studied; but it is sufficiently soluble for absorption
spectroscopy in only a few solvents. Preliminary results indicate that
the A parameter for pentacene has approximately the value 8 x 10^3 cm^{-1},
equal to those for anthracene and tetracene; the data are not adequate
to permit evaluation of B.

^1L_a transitions also are known in the series of aromatic hydrocarbons
in which successive rings are added in a zig-zag pattern. This series
consists of naphthalene, phenanthrene, chrysene, and picene. In this
series, however, the transition designated ^1L_b occurs at lower energy, the
^1L_a transition being the second band of the absorption spectrum. A study
of the solvent shifts of both of these transitions in some members of this
series was undertaken, therefore, in order to determine what regularities,

if any, could be observed.

3. Phenanthrene

Five vibrational maxima of the ^1L_b band of phenanthrene and three
maxima of its ^1L_a band can be located in a wide variety of solvents.
Two of the ^1L_b maxima and all of the ^1L_a band, however, are masked in
many solvents, especially those containing heavy atoms and carbonyl groups.
The positions of these maxima observed in as many as 28 solvents for the
^1L_b band and 16 solvents for the ^1L_a band are reported in the Appendix.
The parameters calculated for these eight bands are listed in Table II, and
the correlations obtained for the 0-0 maxima of both bands are represented
in Figs. 4 and 5. The results for the other components are correlated by
eq. 7 with equal success except for the highest energy maxima of the ^1L_a band.

For this band, the scatter of the data is about twice that for the ^1L_a 0-0 maxima. This band is not well-resolved, and it is difficult to locate its maximum precisely.

Four aspects of the results for the ^1L_b transition should be noted:

1. The magnitudes of the shifts of the ^1L_b band are about one-half of those of the phenanthrene or anthracene ^1L_a bands in the same solvent. This is reflected in the values of the parameters A and B for the ^1L_b and ^1L_a bands.

2. Again, the values obtained for A and B are identical within experimental error for the different vibrational components of this transition.

3. With two exceptions, ethyl ether (13) and t-butyl alcohol (11), all of the observations fall on the best-fit line within experimental error; the precision of the wavelength measurements is indicated by bars on selected data points. The data for the ketones here also appears to be shifted uniformly to lower energies from that for hydrocarbons and alcohols.

4. Because of the relatively small value of B, the magnitude of the maximum value of contribution (1) to the solvent shift (-37 ± 8 cm^{-1} for acetonitrile (28)) is not considerably larger than experimental error. Thus, Weigang and Wild[6] were justified in concluding that phenanthrene shift data reasonably could be fit without considering contributions due to the permanent dipoles of the solvent.

Although the data are limited to a few solvents, the fit obtained for the ^1L_a transition is equally good. The largest deviation is 60 cm^{-1} for 1,2-dichloroethane (44). It should be noted, however, that only solvents belonging to one of the two classes distinguished with anthracene and tetracene can be used in this spectral region. Furthermore, the values obtained for the parameters A and B of the ^1L_a transition are equal to those of ^1L_a transitions in the other molecules studied, independent of the fact that this is the second electronic transition.

4. Chrysene

The resolution of the various vibrational maxima of the ^1L_b and ^1L_a bands of chrysene is less than that of phenanthrene. However, it was possible to obtain useful data for four vibrational maxima of the ^1L_b band in as many as 24 solvents and for three vibrational maxima of the ^1L_a band in 18 solvents. These data are listed in the Appendix, and the correlations obtained for the 0-0 maxima of these bands are represented in Figs. 6 and 7. These plots are virtually identical with those for phenanthrene except for differences in the absolute energies of the transitions.

The values of the A and B parameters for these transitions are listed in Table II. The values obtained for the ^1L_b transition are identical not only for the different vibrational maxima but also with the values obtained for the ^1L_b band of phenanthrene. Similar agreement, within experimental precision, is observed for the parameters of this and other ^1L_a transitions.

5. Naphthalene

Polar solvent shifts of the ^1L_b band of naphthalene are difficult to study for three reasons:

1. Many of the solvents themselves absorb strongly in this region of the spectrum;

2. The 0-0 band of the transition is very weak and appears as a shoulder on a moderately intense vibrational component about 500 cm^{-1} to higher energy; and

3. Other vibrational components of this transition are not clearly separated from the very strong ^1L_a transition which, on the basis of other results described herein, may be shifting to lower energies by twice as much as the ^1L_b band.

Detailed analysis of the absorption band contours, which is beyond the

scope of this work, would be required to separate the combined effects of

the shifts of the two bands at frequencies where both make comparable

contributions to the total extinction coefficient. It appears, however,

that effects due to overlap of these transitions can be neglected to a first

approximation in analyzing shifts of the 0-0+500 cm^{-1} vibrational component

of the ^1L_b transition for most of the hydrocarbons, alcohols, and halogenated

hydrocarbons used in this investigation (carbon tetrachloride excepted,

see below).

The location of this band was determined in 18 solvents in at least

two solutions of different concentrations; the average value found for each

solvent is tabulated in the Appendix. When correlated by eq. 7, these data,

with each determination weighted equally, gave $32,713\pm24$ cm^{-1} for ν_o,

$-2.90\pm0.29 \times 10^3$ cm^{-1} for A, -0.15 ± 0.80 cm^{-1} for B, and the fit represented

in Fig. 8. It is obvious that the data for carbon tetrachloride (46) do not

fit the calculated dependence. Overlap of ^1L_b and ^1L_a bands might account

for this discrepancy; but the data for 1,2-dibromoethane also should deviate

in that case. The origin of this deviation is unknown.

When the data for carbon tetrachloride are omitted from the analysis,

the fit represented in Fig. 9 is obtained; the parameters of eq. 7 obtained

for this fit are listed in Table II. This represents a significant improvement

in the fit, although the magnitudes of A and B are not changed with the

relatively large uncertainty of the data. For either fit, the value of A

agrees well within experimental precision with those for the other ^1L_b

transitions studied. The value of B, however, is apparently smaller for

this transition than for the others from the limited available evidence.

The ^1L_a transition of naphthalene was not studied.

6. Picene

The positions of four vibrational components of the ^1L_b transition of
picene were determined in as many as 30 solvents including several aromatic
solvents. These data are collected in the Appendix, and the values obtained
for the parameters of eq. 7 are listed in Table II. Fig. 10 represents the
correlation obtained for the shift of the O-O band of this transition.
The scatter of the data is slightly greater than that for phenanthrene
and chrysene, and the distinction between the two solvent classes previously
observed is clear. The calculated values of the A and B parameters are the
same as those obtained for phenanthrene and chrysene except that two values
of B appear to be slightly greater for picene. The difference, however,
is not significantly greater than the precision of the measurements.

V. OTHER THEORIES

An alternate approach to the problem of relating polar solvent spectral
shifts to properties of the solvent and chromophore has been developed by
Abe.[4,10] Abe evaluated contribution (2) by using the single term dispersion
formula[11] (eq. 8) for both the ground and excited states of the solute.

$$\langle \Delta E^i_{12} \rangle_{Av} = - \frac{3}{2R^6_{12}} \frac{I_{1i} I_2}{I_{1i}+I_2} \alpha^o_{1i} \alpha^o_2 \qquad (8)$$

Here, $\langle \Delta E^i_{12} \rangle_{Av}$ is the energy shift of the ith state of the solute molecule
(subscript 1) due to the presence of a solvent molecule (subscript 2) at a
distance R_{12} from the solute. I_{1i} is the ionization potential for the solute
in the ith state which, for the excited state is taken to be that of the
ground state less the excitation energy in the vapor phase. This choice
automatically ties the solvent shifts to the vapor phase frequency. I_2 is
the ionization potential of the solvent; and α^o_2 is the static polarizability

of the solvent, which can be evaluated from refractive indices. α_{1i}^o is the

polarizability of the solute in the ith electronic state. R_{12} is evaluated

from the density of the solvent, and the total energy shift of the solute

levels is evaluated by summing over a number of solvent molecules surrounding

the solute by a procedure described in reference 4.

The appearance in the expression for contribution (2) of the static

polarizabilities of the ground and excited states of the solute, which are

rigorously included in the expression for contribution (1), reduces the number

of adjustable parameters by one from those available in eq. 7. Inclusion of

the vapor phase transition frequency in order to evaluate the ionization

potential of the excited state of the solute also reduces the number of

adjustable parameters. Within the framework of the assumption that neither

the ground nor excited states of the solute are polar, Abe's theory reduces

to a one parameter theory in which the adjustable parameter is taken to be

the polarizability of the excited electronic state of the solute.

For comparison with the results previously discussed, the data obtained

in the present investigation for the 0-0 bands of the ^1L_b transition in

phenanthrene and chrysene, the ^1L_a transitions of anthracene and tetracene,

and the 0-0+500 cm^{-1} component of the ^1L_b transition of naphthalene were

analyzed according to Abe's theory to compute the polarizabilities of the

various excited states. Solvent dipole moments, refractive indices, and

densities were taken from the CRC Handbook of Chemistry and Physics; ionization

potentials were taken from Kiser.[12] The results of the computation are

listed in Table III; error estimates are given in terms of the standard

deviations. The values taken for the ground state polarizabilities are

listed for comparison. In general, the computed excited state polarizabilities

are twice those of the ground states. The precision obtained for the

difference between the excited and ground state polarizabilities, the

important factor for solvent shifts, is about 10 per cent; this is comparable to the fit of the shifts obtained by eq. 7.

The one major difference between the fits obtained by the two theories is in the relative magnitudes of the two contributions to the shift. Inevitably, the values of v_o calculated by eq. 7 are 200 to 600 cm^{-1} higher than the observed vapor phase frequencies. It was observed in I that this difference is obtained even for shifts in nonpolar solvents for which contribution (1) is zero. By trying the shifts to the vapor phase transition frequency through Abe's equation for the excited state ionization potential, the estimates of the relative magnitudes of the two contributions are changed. According to Abe's theory, 41% of the shift of the ^1L_a transition of anthracene in acetonitrile arises from contribution (1) while only 10% of the shift is attributed to this origin when the data are analyzed according to eq. 7. Similar differences are obtained for other solvents. Further work is necessary in order to decide which estimate is more nearly correct.

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\#   Contribution No. 2117

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     Chap. 2.

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5.   L. Onsager, J. Am. Chem. Soc. $\underline{58}$, 1486 (1936).

6.   O. E. Weigang and D. D. Wild, J. Chem. Phys. $\underline{37}$, 1180 (1962).

7.   O. L. Davies, Statistical Methods in Research and Production, 3rd ed.

     (Oliver & Boyd, London, 1957), Chap. 8.

8.   In I, it was indicated that the proposed theory might not be applicable

     to solutions in aromatic solvents due to the possible importance of other,

     e.g. charge transfer, interactions. This remark was included in part

     because it was not possible to fit literature data on polar solvent

     shifts of the $^{1}L_{b}$ transition of naphthalene in aromatic solvents by

     the method then being used; even the sign of the B constant could not

     be determined. It is shown later that this transition of this solute

     is an exceedingly poor choice in order to test polar solvent shift

     theories. Shifts of the anthracene and picene spectra in aromatic

     solvents reported here are found to be in very satisfactory agreement

     with the present theory.

9.   See J. N. Murrell, The Theory of the Electronic Spectra of Organic

     Molecules (Wiley, New York, 1963), p. 94.

10. T. Abe, Y. Amake, T. Nishioka, and H. Azumi, Bull. Chem. Soc. Japan $\underline{39}$,

     845 (1966). Eq. 1 of this paper is the correct expression for the

     polar solvent shifts of the spectra of nonpolar molecules within the

     framework of Abe's model. It differs slightly from the more general

expression in Eq. 20 of Ref. 4 from which the term corresponding to contribution (1) unfortunately was omitted.

11. See, e.g., H. Marganeau, Rev. Mod. Phys. 11, 1 (1939), Eq. 21.

12. R. W. Kiser, U. S. Atomic Energy Comm. Report TID-6142 (1960).

Table I: List of Solvents Including a Key to the Illustrations

Solvent	Number	$\dfrac{n^2 - 1}{2n^2 + 1}$	$\dfrac{(2\epsilon+n^2)(\epsilon-n^2)}{\epsilon(n^2+2)}$ ± 0.02
Hydrocarbons (●)			
Pentane	1	0.1799[a]	0.00
Hexane	2	0.1862[a]	0.00
Heptane	3	0.1908[a]	0.00
Nonane	4	0.1970[a]	0.00
Decane	42	0.1993[a]	0.00
Undecane	5	0.2010[a]	0.00
Tetradecane	40	0.2049[a]	0.00
Hexadecane	43	0.2071[a]	0.00
1,5-Cyclooctadiene	51	0.2253[a]	0.00
Benzene	61	0.2276[b]	0.00
p-Xylene	62	0.2274[b]	0.00
Cyclohexane	45	0.2050[b]	0.00
Alcohols (o)			
Methanol	6	0.1699[b]	16.81
Ethanol	7	0.1817[b]	12.09
1-Propanol	8	0.1900[b]	9.72
2-Propanol	9	0.1872[b]	8.85
n-Butanol	10	0.1949[b]	8.09
t-Butanol	11	0.1909[b]	7.50
i-Butanol	56	0.1940[b]	8.41
s-Butanol	57	0.1940[b]	7.44
n-Amyl alcohol	12	0.1985[b]	6.40
Ethylene glycol	49	0.2044[b]	18.14
Benzyl alcohol	63	0.2387[b]	5.35

Ketones (◓)

Acetone	16	0.1804^b	10.24
Butanone	18	0.1883^b	8.93
2-Pentanone	19	0.1914^b	7.28
3-Pentanone	41	0.1930^b	8.07
5-Hexen-2-one	20	0.2024^b	6.94
2-Heptanone	21	0.1974^c	5.40
3-Heptanone	22	0.1974^c	5.91
4-Heptanone	23	0.1976^b	5.76
2-Octanone	24	0.2006^b	4.60
2-Nonanone	25	0.2015^c	4.38
2-Undecanone	26	0.2053^b	3.52
Acetophenone	64	0.2372^b	7.37

Chlorinated Hydrocarbons (▣)

Carbon tetrachloride	46	0.2160^b	0.00
Chloroform	47	0.2107^b	1.62
1,2-Dichloroethane	44	0.2100^b	4.45
1,1,1-Trichlorethane	52	0.2069^b	3.05
1-Chloropropane	53	0.1911^b	3.31
1-Chlorobutane	54	0.1956^b	3.10
1-Chloropentane	55	0.1992^b	2.66
Chlorobenzene	65	0.2343^b	1.84

Brominated Hydrocarbons (■)

1,2-Dibromoethane	37	0.2382^b	1.38
1-Bromobutane	36	0.2085^b	2.81
Bromobenzene	66	0.2450^b	1.63
1-Bromonaphthalene	59	0.2693^b	1.12

Iodinated Hydrocarbons (□)

Iodomethane	38	0.2353[c]	2.51
1-Iodobutane	39	0.2273[b]	2.20

Nitriles (X)

Acetonitrile	28	0.1756[b]	19.18
n-Valeronitrile	29	0.1919[b]	8.30
Benzonitrile	60	0.2357[b]	11.03

Ethers (◑)

Ethyl ether	13	0.1770[b]	1.59
n-Butyl ether	14	0.1948[b]	0.74
Dioxane	15	0.2028[b]	0.14

Acids (▲)

Acetic Acid	30	0.1851[b]	2.54
Butyric Acid	27	0.1948[b]	0.68

Esters (△)

Ethyl Acetate	31	0.1849[b]	2.47
Amyl acetate	32	0.1955[b]	1.70

Aldehydes (+)

Propanaldehyde	48	0.1821[b]	9.06
n-Butyraldehyde	50	0.1896[b]	6.28

Nitrates (▽)

Nitromethane	33	0.1887[b]	17.85
Nitroethane	34	0.1916[b]	13.77
1-Nitropropane	35	0.1952[b]	11.18

References: a) Phillips Petroleum Reference Data for Hydrocarbons

b) CRC Handbook of Chemistry and Physics

c) Reference 6

Table II: Best Fit Values of Parameters in Solvent

Shift Expression, Eq. 7.

Transition	Number of Solvents Studied	ν_0 (ν for vapor) cm^{-1}	$10^{-3} \times A$ cm^{-1}	B cm^{-1}
Naphthalene				
^1L_b	19	32,684±16 (32,458)	-2.72±0.19	-0.6±0.5
Anthracene				
^1L_a	46	27,917±37 (27,590)	-6.80±0.24	-7.3±0.8
	45	29,358±37	-6.87±0.25	-7.3±0.8
	45	30,873±41	-7.28±0.27	-8.1±0.9
	31	32,214±38	-6.84±0.32	-7.0±0.9
Phenanthrene				
^1L_b	28	29,493±11 (29,163)	-3.02±0.15	-1.9±0.4
	28	30,108±13	-2.78±0.17	-1.5±0.5
	27	30,914±19	-3.14±0.26	-0.8±0.8
	20	31,560±11	-3.07±0.15	-1.7±0.4
	19	32,244±11	-2.77±0.15	-1.6±0.5
^1L_a	16	35,796±30	-8.45±0.72	-8.5±1.1
	16	37,065±31	-7.64±0.77	-7.8±1.2
	16	37,928±37	-7.72±0.90	-4.3±1.5
Tetracene				
^1L_a	39	22,675±38 (22,220)	-7.43±0.48	-6.8±1.3

Chrysene

^1L_b	24	$28,295\pm9$ $(28,250)$	-3.09 ± 0.15	-2.3 ± 0.4
	24	$28,888\pm10$	-2.92 ± 0.16	-1.9 ± 0.4
	24	$29,150\pm10$	-3.12 ± 0.16	-1.5 ± 0.4
	24	$29,651\pm11$	-2.96 ± 0.19	-2.2 ± 0.4
^1L_a	18	$32,865\pm33$	-8.21 ± 0.54	-6.7 ± 1.3
	18	$34,277\pm37$	-8.35 ± 0.60	-7.4 ± 1.4
	18	$35,631\pm31$	-8.38 ± 0.50	-8.5 ± 1.2

Picene

^1L_b	30	$27,292\pm14$	-3.28 ± 0.14	-3.5 ± 0.5
	26	$27,842\pm22$	-3.06 ± 0.28	-2.0 ± 0.8
	29	$28,092\pm23$	$-3.04\pm-.23$	-2.3 ± 0.8
	30	$28,661\pm14$	-3.23 ± 0.14	-3.3 ± 0.5

Table III: Excited State Polarizabilities Calculated

by Abe's Theory

Solute	Transition	Number of Solvents	$\alpha(A^3)$	
			Excited State	Ground State
Naphthalene	^1L_b	11	32.1 ± 1.8	17.1
Phenanthrene	^1L_b	14	40.6 ± 1.9	23.8
Chrysene	^1L_b	14	61.2 ± 3.9	30.6
Anthracene	^1L_a	22	59.3 ± 4.1	23.8
Tetracene	^1L_a	19	72.4 ± 5.0	30.6

CAPTIONS

Fig. 1.   A plot of the experimental frequency of the 0-0 band of the ^1L_a
transition of tetracene versus the function $(n^2-1/2n^2+1)$ for
39 solvents, where n is the refractive index of the solvent.
The lines represent least squares fits of the correlation between
these variables for the hydrocarbons _____, halogenated
hydrocarbons ___ _ ___ _ ___, alcohols __ __ __ __, and
ketones _ _ _ _ _.

Fig. 2.   A plot of the experimental frequency of the 0-0 band of the ^1L_a
transition of tetracene versus the frequency shift calculated
from the best fit of eq. 7 to these data. The solid line represents
the best fit.

Fig. 3.   A plot of the experimental frequency of the 0-0 band of the ^1L_a
transition of anthracene versus the frequency shift calculated
from the best fit of eq. 7 to these data. The solid line represents
the best fit.

Fig. 4.   A plot of the experimental frequency of the 0-0 band of the ^1L_b
transition of phenanthrene versus the frequency shift calculated
from the best fit of eq. 7 to these data. The solid line represents
the best fit.

Fig. 5.   A plot of the experimental frequency of the 0-0 band of the ^1L_a
transition of phenanthrene versus the frequency shift calculated
from the best fit of eq. 7 to these data. The solid line represents
the best fit.

Fig. 6.   A plot of the experimental frequency of the 0-0 band of the ^1L_b
transition of chrysene versus the frequency shift calculated
from the best fit of eq. 7 to these data. The solid line represents
the best fit.

Fig. 7.   A plot of the experimental frequency of the 0-0 band of the ^1L_a

transition of chrysene versus the frequency shift calculated

from the best fit of eq. 7 to these data. The solid line represents

the best fit.

Fig. 8.   A plot of the experimental frequency of the 0-0 ✦ 500 cm^{-1} band of

the ^1L_b transition of naphthalene versus the frequency shift

calculated from the best fit of eq. 7 to these data, which include

the data for carbon tetrachloride. The solid line represents the

best fit.

Fig. 9.   A plot of the experimental frequency of the 0-0 ✦ 500 cm^{-1} band

of the ^1L_b transition of naphthalene versus the frequency shift

calculated from the best fit of eq. 7 to these data, which do

not include data for carbon tetrachloride. The solid line

represents the best fit.

Fig. 10.   A plot of the experimental frequency of the 0-0 band of the ^1L_b

transition of picene versus the frequency shift calculated from

the best fit of eq. 7 to these data. The solid line represents

the best fit.

APPENDIX

Table of Frequencies of Absorption Band Maxima

Solute and Transition	Solvent	Absorption Maxima (cm^{-1})			
Naphthalene ^1L_b	Hexane	32, 172			
	Heptane	175			
	Methanol	193			
	Ethanol	180			
	1-Propanol	164			
	n-Butanol	158			
	n-Amyl alcohol	144			
	Dioxane	144			
	Allyl alcohol	134			
	1-Bromobutane	120			
	1,2-Dibromoethane	031			
	Tetradecane	123			
	Cyclohexane	154			
	Carbon Tetrachloride	025			
	Chloroform	090			
	1,5-Cyclooctadiene	092			
	i-Butanol	170			
	s-Butanol	170			
Anthracene ^1L_a	Pentane	26, 721	28, 145	29, 568	30, 998
	Hexane	681	106	530	959
	Heptane	648	078	507	935
	Nonane	608	032	464	897
	Undecane	588	003	434	859

Solute and Transition	Solvent	Absorption Maxima			
Anthracene ^1L_a	Methanol	26, 656	28, 078	29, 516	30, 926
	Ethanol	620	054	477	908
	1-Propanol	594	020	455	869
	n-Butanol	567	27, 996	429	840
	n-Amyl alcohol	553	980	407	-
	Ethyl ether	664	28, 090	512	945
	Acetone	579	007	434	859
	Allyl alcohol	504	27, 933	369	788
	1-Pentanone	568	28, 009	429	-
	2-Heptanone	509	27, 945	382	-
	3-Heptanone	518	950	382	-
	2-Octanone	511	941	378	-
	Acetonitrile	589	28, 019	446	864
	Ethyl acetate	602	030	459	878
	Nitromethane	483	27, 914	265	-
	Nitroethane	501	925	355	-
	1-Nitropropane	501	925	385	-
	1-Bromobutane	476	910	108	534
	1,2-Dibromoethane	244	674	108	-
	Tetradecane	564	992	404	845
	3-Pentanone	548	988	404	-
	1,2-Dichloroethane	407	841	268	696
	Cyclohexane	596	28, 023	455	878
	Carbon tetrachloride	389	27, 812	240	661
	Chloroform	399	832	248	694
	Propanaldehyde	536	964	390	-
	Ethylene glycol	406	832	260	698
	n-Butyraldehyde	518	940	445	883

Solute and Transition	Solvent	Absorption Maxima				
Anthracene ^1L_a	1,1,1-Trichloroethane	26, 492	27, 935	29, 357	30, 772	
	1-Chloropropane	591	28, 014	473	865	
	1-Chlorobutane	563	27, 993	426	854	
	1-Chloropentane	545	974	415	855	
	1-Bromonaphthalene	109	541	28, 823	-	
	Benzonitrile	278	696	29, 120	-	
	Benzene	392	816	257	684	
	Benzyl alcohol	272	705	143	592	
	Acetophenone	272	-	-	-	
	Bromobenzene	272	685	133	571	
Phenanthrene ^1L_b	Pentane	28,941	29,603	30,349	30,998	31,746
	Hexane	931	590	331	988	731
	Heptane	921	586	326	979	715
	Nonane	905	568	303	960	706
	Methanol	935	599	335	993	726
	Ethanol	923	577	321	979	726
	1-Propanol	918	590	321	960	721
	n-Butanol	897	560	303	950	696
	t-Butanol	931	603	326	979	726
	n-Amyl alcohol	887	560	294	950	691
	Acetone	927	586	331	-	-
	Allyl alcohol	877	533	276	941	675
	Butanone	904	564	312	-	-
	2-Pentanone	889	551	289	-	-
	2-Heptanone	877	533	285	-	-
	3-Heptanone	873	546	276	-	-
	4-Heptanone	881	542	=	=	-

Solute and Transition	Solvent	Absorption Maxima				
Phenanthrene ^1L_b	2-Octanone	28,866	29,529	30,266	-	-
	Acetonitrile	929	603	432	30,989	-
	1-Bromobutane	858	525	256	911	31,660
	1,2-Dibromoethane	760	438	153	812	576
	Tetradecane	889	555	294	941	686
	3-Pentanone	885	546	289	-	-
	Decane	902	560	298	950	696
	Hexadecane	881	533	280	936	676
	1,2-Dichloroethane	852	516	257	912	646
^1L_a	Pentane	34,251	35,684	36,538		
	Hexane	213	607	504		
	Heptane	178	616	482		
	Nonane	131	563	401		
	Methanol	172	600	500		
	Ethanol	158	585	482		
	1-Propanol	178	595	491		
	n-Butanol	099	552	382		
	n-Amyl alcohol	061	494	391		
	Allyl alcohol	003	443	332		
	Acetonitrile	164	578	504		
	Decane	106	538	306		
	1,2-Dichloroethane	33,916	354	253		
	Cyclohexane	34,102	538	395		
	Ethylene glycol	33,909	364	286		

Solute and Transition	Solvent	Absorption Maxima			
Chrysene ^1L_b	Pentane	27,732	28,365	28,588	29,108
	Hexane	724	341	567	104
	Heptane	709	333	555	095
	Nonane	693	305	539	078
	Methanol	724	361	580	104
	Ethanol	709	337	563	091
	1-Propanol	693	325	551	078
	n-Butanol	685	313	539	061
	n-Amyl alcohol	674	301	531	057
	Acetone	705	337	563	078
	Allyl alcohol	655	289	514	040
	Butanone	678	309	543	053
	2-Pentanone	674	309	543	061
	4-Heptanone	659	293	514	044
	2-Octanone	651	285	510	036
	Acetonitrile	709	353	563	087
	1-Bromobutane	643	276	490	023
	1,2-Dibromoethane	544	197	389	28,927
	Tetradecane	670	289	502	29,052
	Decane	685	305	535	061
	Hexadecane	663	289	506	044
	Ethylene glycol	632	237	498	019

Solute and Transition	Solvent	Absorption Maxima			
Chrysene ^1L_a	Pentane	31,287	32,783	34,170	
	Hexane	334	735	088	
	Heptane	298	687	041	
	Nonane	252	663	33,982	
	Methanol	361	720	34,045	
	Ethanol	289	662	029	
	1-Propanol	260	666	33,932	
	2-Propanol	299	670	34,043	
	n-Butanol	224	598	33,925	
	Ethyl ether	318	696	34,067	
	Allyl alcohol	170	554	33,844	
	Acetonitrile	293	660	993	
	1,2-Dibromoethane	30,864	240	619	
	Decane	31,237	616	941	
	1,2-Dichloroethane	094	439	812	
	Cyclohexane	253	616	928	
	Ethylene glycol	039	434	787	
Picene ^1L_b	Pentane	26,695	27,274	27,544	28,082
	Hexane	688	274	525	066
	Heptane	681	263	514	050
	Nonane	649	241	495	035
	Methanol	674	304	541	058
	Ethanol	660	270	503	043
	1-Propanol	652	259	461	019
	n-Butanol	631	263	488	019
	n-Amyl alcohol	617	226	495	007

Solute and Transition	Solvent	Absorption Maxima			
Picene ^1L_b	Acetone	26,645	27,211	27,571	28,019
	Butanone	624	263	487	019
	2-Pentanone	617	233	503	27,999
	4-Heptanone	610	226	472	987
	2-Octanone	596	203	507	28,003
	Acetonitrile	660	285	541	039
	1-Bromobutane	596	196	439	27,968
	1,2-Dibromoethane	490	097	349	875
	Tetradecane	631	211	465	28,015
	Decane	652	233	502	039
	Hexadecane	617	189	450	003
	1,2-Dichloroethane	575	211	435	27,956
	Ethylene glycol	578	122	382	964
	Benzonitrile	490	-	375	878
	p-Xylene	546	-	409	925
	Benzyl alcohol	483	122	352	870
	Chlorobenzene	518	130	382	902
	Bromobenzene	480	-	360	855