

# Oscillator Strengths for Electronic Spectra of Conjugated Molecules from Transition Gradients

## III. Polyacenes

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Transition dipole moments for the  $N - V_1$  and  $N - V_2$  transitions of eight polyacenes calculated from transition gradients, rather than the more conventional transition moments, are in good agreement with experiment. Integration over the complete experimental absorption curve yields a quantity relatively independent of overlapped bands, "intensity stealing", configuration interaction (CI) etc. Use of this integrated intensity shows unambiguously that the transition gradient is to be preferred over the transition dipole if simple  $\pi$ -electron wavefunctions are to be used for calculating absorption strength.

Die Übergangsdipolmomente für die  $N - V_1$ - und  $N - V_2$ -Übergänge bei acht Polyacenen, die mit Hilfe der Übergangsgradienten berechnet wurden, zeigen eine gute Übereinstimmung mit dem Experiment. Integration über die gesamte experimentelle Absorptionskurve führt zu einer Größe, die relativ unabhängig von Bandüberlappungen, Konfigurationswechselwirkung u. a. ist. Wird diese Größe benutzt, zeigt sich, daß die Übergangsgradienten bei einem Ansatz mit einfachen  $\pi$ -Wellenfunktionen zur Berechnung der Absorptionsstärke den Übergangsmomenten vorzuziehen sind.

Les forces oscillatrices des transitions  $N - V_1$  et  $N - V_2$  de huit polyacènes calculées à partir des gradients de transition, plutôt qu'à partir des moments de transition, sont en bon accord avec l'expérience. L'intégration sur toute la courbe d'absorption expérimentale fournit une quantité relative indépendante du recouvrement des bandes, de l'interaction de configuration, etc. L'emploi de cette intensité intégrée montre d'une manière non ambiguë que le gradient de transition doit être préférentiellement utilisé si l'on veut calculer des intensités d'absorption à partir de fonctions d'ondes d'électrons  $\pi$ .

It has often been remarked that the oscillator strengths calculated from  $\pi$ -electron wavefunctions commonly exceed experimental values by a factor varying from 1 to 5. Listing the ratio of calculated to observed oscillator strengths, some randomly chosen examples are ethylene [1] (1.1 : 1), 18-annulene [2] (2.5 : 1) and tetracene [3] (4.7 : 1). This gross failure is in striking contrast to the wide success of the  $\pi$ -electron model in accounting for a variety of physical measurements and raises the spectre that there is some glaring error in the wavefunctions. Moreover since intensity is, after energy, the most important spectroscopic datum, the failure of  $\pi$ -wavefunctions to predict absolute intensity is of practical concern. The calculations are useless for providing a critique on absolute intensity data. Moreover, predictions of relative changes, such as might occur on substitution or dimerization, cannot be taken too seriously when the model fails so grossly in predicting absolute values.

In this paper we follow up previous studies in Papers I [4] and II [5] and show that the transition dipole velocity gives consistently better predictions of intensity than the transition dipole itself. We shall report studies on eight polyacenes and shall show the results are sufficiently good that they can be used to criticize experimental data.

### General Formulas

#### A. Relation of Operators to Data

We begin by defining transition moment and transition gradient operators as follows:

$$R_{aA} = \left\langle \Psi_a \left| \sum_j r_j \right| \Psi_A \right\rangle, \quad (1)$$

$$H_{aA} = \left\langle \Psi_a \left| \sum_j \nabla_j \right| \Psi_A \right\rangle. \quad (2)$$

The experimental measure of a spectrum is the optical cross section  $\sigma$  defined as

$$\ln(I_0/I) = \sigma nd, \quad (3)$$

where  $I_0$  is the incident intensity and  $I$  is the transmitted intensity through a sample  $d$  cm thick with  $n$  absorbers per  $\text{cm}^3$ . An equivalent measure is the molar extinction coefficient defined as

$$\log_{10}(I_0/I) = \epsilon cd \quad (4)$$

where  $c$  is the concentration in moles per liter. Molecular electronic transitions  $\Psi_a \rightarrow \Psi_A$  are not sharp but occur over a range of wave numbers  $\tilde{\nu}$  which may be more or less broad depending on such things as temperature, solvent, concentration, as well as intrinsic features of the molecule and the transition in question. In a case where the transition is not overlapped by other absorption bands, we can relate  $R_{aA}$  and  $H_{aA}$  to the optical cross section as<sup>1</sup>

$$|R_{aA}|^2 = (3\hbar c/4\pi^2 e^2) \int \sigma(\tilde{\nu}) d \ln \tilde{\nu}, \quad (5)$$

$$|H_{aA}|^2 = (3m^2 c^3/\hbar e^2) \int \sigma(\tilde{\nu}) \tilde{\nu} d\tilde{\nu}, \quad (6)$$

where  $R_{aA}$  is in cms and  $H_{aA}$  is in  $\text{cm}^{-1}$ . In these expressions we have a purely calculated number on the left and an experimental number on the right.

Another method of relating calculated to experimental intensities is by means of the oscillator strength. We can, following Papers I and II, define two theoretical oscillator strengths as

$$f_1 = (2/3) |R_{aA}|^2 (E_A - E_a) (m/\hbar^2), \quad (7)$$

$$f_2 = (2/3) |H_{aA}|^2 (E_A - E_a)^{-1} (\hbar^2/m), \quad (8)$$

where we assume  $E_A > E_a$ . These can be compared to an experimental oscillator strength

$$f = (mc^2/\pi e^2) \int \sigma(\tilde{\nu}) d\tilde{\nu}. \quad (9)$$

Many authors have used for  $f_1$  and  $f_2$  quantities calculated with theoretical values for  $R_{aA}$  or  $H_{aA}$  and experimental values for the energy difference. Such oscillator strengths have been called "semi-empirical." Their use amounts, in effect, to making comparisons based on Eqs. (5) and (6). Hansen [6] has suggested

<sup>1</sup> The constants in Eqs. (5), (6), (9) are  $(3\hbar c/4\pi^2 e^2) = 10.4137$ ;  $(3m^2 c^3/\hbar e^2) = 2.75721 \times 10^{23}$ ;  $(mc^2/\pi e^2) = 1.12966 \times 10^{12}$ .

a mixed oscillator strength

$$f_3 = 2/3 R_{aA} \cdot \Pi_{aA} \quad (9')$$

Because much empirical data is tabulated in terms of oscillator strengths, we shall make comparisons with  $f_1$  and  $f_2$ , however, using experimental energies. This is, except for a slightly different averaging procedure, equivalent to using (5) and (6). We shall also make use of (5) and (6) directly. Since our results show that  $f_1$  is uniformly high and  $f_2$  uniformly of the right size,  $f_3$  should clearly give a result somewhere in between, and we have not considered it.

### B. Polyacenes: First Comparisons

For a simple oscillator strength comparison we have considered the lowest two excited states of the polyacenes:  $N \rightarrow V_1$  and  $N \rightarrow V_2$  in Mulliken's notation or  ${}^1L_a \leftarrow {}^1A$  and  ${}^1B_b \leftarrow {}^1A$  in Platt's. If we call the top filled orbitals  $n-1$  and  $n$  and the lowest empty orbitals  $n^1$  and  $(n-1)^1$ , then a simple representation for the lower excited state is the singly excited state  $nn^1$ . However, the second excited state shows considerable configuration interaction. We shall as a first approximation treat it as the normalized linear combination  $[(n-1)n^1 + n(n-1)^1]/\sqrt{2}$ . We have expanded the molecular orbitals into linear combinations of Slater  $2p\pi$  orbitals on each carbon. The orbital coefficients have been obtained from a simple Hückel calculation [7], and the exponent of the orbital was taken as  $\zeta = 1.59$ . For geometry we used regular hexagons with sides 1.39 Å. The state integrals for  $R_{aA}$  and  $\Pi_{aA}$  reduce to one electron orbital integrals  $(i|r|j)$  or  $(i|\bar{V}|j)$ , where  $i$  and  $j$  refer to molecular orbitals. These, in turn, reduce to integrals over atomic orbitals.  $R_{aA}$  contains one and two center atomic integrals while  $\Pi_{aA}$  contains only two center terms. All the two center integrals were kept in our calculation. The integrals over the atomic orbitals were computed using slightly modified versions of subroutines originally written by R. L. Ake. The molecular orbitals were not normalized. Our semi-empirical values for  $f_1$  and  $f_2$  based on these calculations are given in Table 1.

Table 1. Oscillator strengths for some linear polyacenes

Molecule	Transition <sup>a</sup>	Energy (cm <sup>-1</sup> )	$f_1$ <sup>b</sup>	$f_2$	Expt. osc. strength	Klevens Platt
Naphthalene	$N - V_1({}^1L_a)$	36400	0.53	0.18	0.11 <sup>c</sup>	0.18
	$N - V_2({}^1B_b)$	45400	2.10	0.87	1.2 <sup>c</sup>	1.70
Anthracene	$N - V_1({}^1L_a)$	26700	0.49	0.13		0.10
	$N - V_2({}^1B_b)$	39000	2.77	1.21	1.6 <sup>d</sup>	2.28
Tetracene	$N - V_1({}^1L_a)$	21000	0.46	0.09		0.08
	$N - V_2({}^1B_b)$	36700	3.40	1.41		1.85
Pentacene	$N - V_1({}^1L_a)$	20000	0.43	0.05		0.08
	$N - V_2({}^1B_b)$	32300	3.11	1.71		2.2

<sup>a</sup> H. B. Klevens and J. R. Platt. Ref. [8].

<sup>b</sup> Includes one-center terms  $\int \chi_i^* \chi_i$  only.

<sup>c</sup> A. Bree and T. Thirunamachandran. Ref. [9].

<sup>d</sup> DMS UV Atlas of Organic Compounds. Ref. [12].

A major source for empirical oscillator strengths of the polyacenes has been the work of Klevens and Platt [8]. Their numbers calculated from Eq. (9), are given in Table 1. More recent studies by Bree and Thirunamachandran [9] and by Ferguson *et al.* [10] show disagreements with their work.

One way of checking the revised experimental numbers for the  ${}^1B_b \leftarrow {}^1A$  transitions in naphthalene and anthracene is to plot oscillator strength versus polyacene chain length. Fig. 1 shows that the newer points fall nicely on a straight line expected from the vibrating plate analogy, while those of Klevens and Platt are rather too high. For the  ${}^1L_a \leftarrow {}^1A$  transition in naphthalene, we prefer the newer value of 0.11 to the older figure of 0.18 on the basis of our own integration of data from the new U.V. Atlas [12] which yielded  $f = 0.11$ .

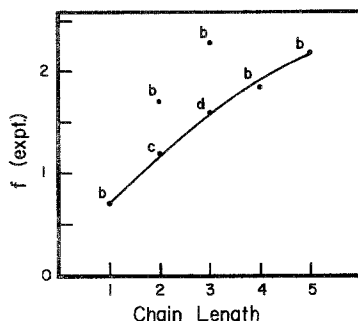


Fig. 1. Expt. oscillator strengths for the  ${}^1B_b \leftarrow {}^1A$  long-axis polarized absorption band of some linear polyacenes. Chain length in units of the benzene ring. <sup>b</sup>From Klevens and Platt, Ref. [8]. <sup>c</sup>From Bree and Thirunamachandran, Ref. [9]. <sup>d</sup>From Ferguson *et al.*, Ref. [10]

Comparison of calculated values of  $f_1$  and  $f_2$  with experimental values of  $f$  for the lower energy  ${}^1L_a \leftarrow {}^1A$  band shows that  $f_2$  gives the right order of magnitude while  $f_1$  can be grossly in error. For the transition  ${}^1B_b \leftarrow {}^1A$  the picture is not so clear. However, when we replace Platt and Klevens data by more modern values, we see that  $f_2$  gives about three-fourths of the experimental value while  $f_1$  is large by a factor of 1.5 to 2. In this case  $f_2$  would again seem to give a better measure of intensity.

### C. Variant Calculations

It might be argued that not all two-center integrals should be kept in calculations based on ZDO Hückel wavefunctions. Hansen has analyzed the integrals expressed in terms of Löwdin orthogonalized orbitals. He obtains the equations for nearest neighbor integrals:

$$\begin{aligned} \langle \lambda_p | r | \lambda_{p+1} \rangle &= \langle \chi_p | r | \chi_{p+1} \rangle - \frac{1}{2} S_{p,p+1} [\langle \chi_p | r | \chi_p \rangle + \langle \chi_{p+1} | r | \chi_{p+1} \rangle] \\ \langle \lambda_p | \nabla | \lambda_{p+1} \rangle &= \langle \chi_p | \nabla | \chi_{p+1} \rangle. \end{aligned}$$

In these expressions  $\lambda_p$  represents the  $p^{\text{th}}$  orthogonalized orbital,  $\chi_p$  the corresponding Slater orbital, while  $S_{p,p+1}$  is the overlap. For one center terms  $\langle \lambda_p | r | \lambda_p \rangle = R_p$  while  $\langle \lambda_p | \nabla | \lambda_p \rangle = 0$ . However, for the important case that  $\chi_p$  and  $\chi_{p+1}$  are  $2p\pi$

orbitals with identical exponents,  $\langle \lambda_p | r | \lambda_{p+1} \rangle = 0$ . Thus Hansen's formulas suggest that for a ZDO calculation, only the one-center terms should be kept for  $R_{aA}$  giving an answer correct to  $O(S^2)$  while  $\Pi_{aA}$  will be correct to the same order when nearest neighbor terms are evaluated.

In our calculation we kept all two center terms in both. The relative magnitudes of integrals over the one-center, nearest neighbor, next nearest neighbors are roughly in the ratio of 1:0.25:0.04 for  $R_{aA}$  and 0:0.19:0.04 for  $\Pi_{aA}$ . However, when the phase of contributions and distribution of A.O. coefficients is taken into account, the effect of keeping only one-center terms for  $R_{aA}$  and two-center nearest neighbor terms for  $\Pi_{aA}$  turns out to be a simple, uniform 10 per cent increase in both theoretical plots at the  $2.5\beta$  level. (See next section.) For such a method,  $\beta$  values would be chosen somewhat differently, but the change would not exceed ( $-$ ) 10 per cent. Thus, our conclusions would be unaltered by this variation of the procedure.

It is clear that the effect of changing the exponent  $\zeta$  has no effect on  $R_{aA}$  calculated in the ZDO approximation and therefore only a small effect is to be

Table 2. Effect of changing  $\zeta$  on oscillator strengths in naphthalene<sup>a</sup>

$\zeta$	${}^1L_a \leftarrow {}^1A$		${}^1B_b \leftarrow {}^1A$	
	$f_1$	$f_2$	$f_1$	$f_2$
1.2929	0.497	0.274	2.545	1.330
1.44	0.507	0.249	2.395	1.178
1.5679	0.497	0.221	2.273	1.033

<sup>a</sup> Molecular orbitals derived from an extended Hückel program written by M. Zerner.

expected in any method where the wavefunctions are not renormalized in the new basis set. However, properly normalized wavefunctions obtained from M. C. Zerner's [13] extended Hückel program were such as to render calculated oscillator strengths somewhat sensitive to changes in  $\zeta$ . Table 2 lists  $f_1$  and  $f_2$  values calculated for the  ${}^1L_a \leftarrow {}^1A$  and  ${}^1B_b \leftarrow {}^1A$  naphthalene transitions. It can be seen that quite large percentage changes in  $f$  occur. Despite the variation, the  $f_1$  values are still in gross disagreement with experiment while the  $f_2$  values merely get a little better or a little worse.

The incorporation of X-ray geometries into the calculations would have been a final step were we interested in obtaining specific predictions for individual molecules. Since our aim was to determine whether  $\Pi_{aA}$  or  $R_{aA}$  is superior, we are not concerned about the small differences introduced by variation in bond lengths and angles.

#### D. Cumulative Integrated Intensity

The reader is bound to object that the comparisons of the previous section were based on wavefunctions that are far too naive. Indeed, if we concentrate our attention on the question of whether  $f_1$  or  $f_2$  gives a better estimate of intensity,

a comparison band for band is treacherous. First, we cannot be sure within the framework of semi-empirical  $\pi$ -electron theory that more refined calculations actually improve the wavefunction. Moreover there are serious experimental problems in extracting oscillator strengths for individual electronic transitions from a plot of  $\sigma(\tilde{\nu})$ . Bands may overlap, and their origins and cut offs may be ill defined. They may even be misidentified!

To get around these problems we shall reformulate our question in a form that allows a less ambiguous answer. We suppose that we describe our ground state as a closed shell of  $\pi$ -electrons and our excited states as linear combinations of singly excited states  $nn^1$ ,  $n(n-1)^1$ ,  $(n-1)n^1$ ,  $(n-1)(n-1)^1$ , etc. In a naive Hückel model each one of these transitions occurs at an energy  $x\beta$ , where  $\beta$  is the resonance integral with value  $\sim 23,000 \text{ cm}^{-1}$ . We can then define

$$R^2(x)_{\text{th}} = \sum_0^x |R_{aA}|^2, \quad (10)$$

$$\Pi^2(x)_{\text{th}} = \sum_0^x |\Pi_{aA}|^2, \quad (11)$$

where we mean by  $\sum_0^x$  to sum over all Hückel transitions whose energy is less than  $x\beta$ . The quantities  $R^2(x)$  and  $\Pi^2(x)$  will then start at zero and increase in steps at each transition energy. These theoretical quantities can then be compared respectively to experimental quantities

$$R^2(x)_{\text{exp}} = (10.4137) \int_0^{x\beta} \sigma(\tilde{\nu}) d \ln \tilde{\nu}, \quad (10')$$

$$\Pi^2(x)_{\text{exp}} = (2.75721 \times 10^23) \int_0^{x\beta} \sigma(\tilde{\nu}) \tilde{\nu} d \tilde{\nu}. \quad (11')$$

The experimental functions, like the calculated, increase monotonically but are smooth. We can then compare (10') with (10) and (11') with (11) as functions of  $x$ . We have allowed one parameter in the comparison. We have chosen  $\beta$  for each molecule to obtain best fit. The results are plotted in Fig. 2. The theoretical sums are taken out to about  $3\beta$ . The experimental integrals are terminated by the available data at  $55,000 \text{ cm}^{-1}$ . It can be seen that the  $\beta$  values used are consistent with the variation in  $\beta$  values that already appear in the literature. Aside from this parameter our comparison is absolute.

The results of our study are quite unambiguous. Except for naphthalene, where there is a small spectral region in which the experimental and theoretical values of  $R^2(x)$  are in reasonable agreement, in all other cases  $R^2(x)$  is seriously in error while  $\Pi^2(x)$  shows moderately good agreement.

It is easy to see that the foregoing procedure deals with overlapping bands in an exact fashion because we are comparing totals of intensity in a given spectral range. Similarly, as we extend the upper limit  $x$  sufficiently far into the U.V., the summation should eventually become invariant to any reasonable degree of vibronic coupling. Furthermore, it is relatively easy to show that the procedure

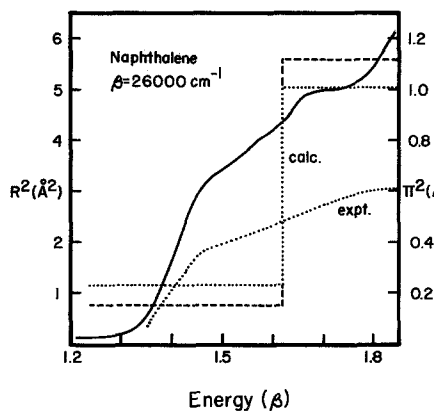


Fig. 2a

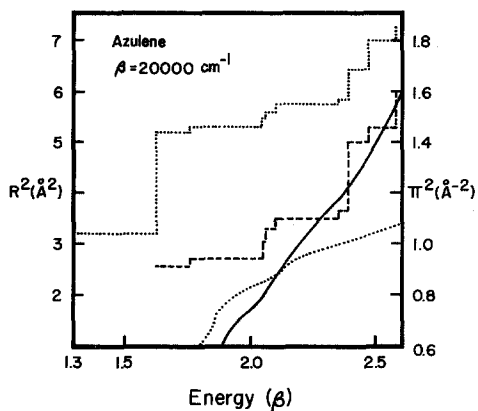


Fig. 2b

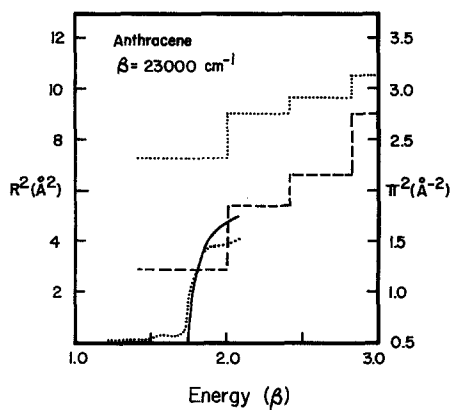


Fig. 2c

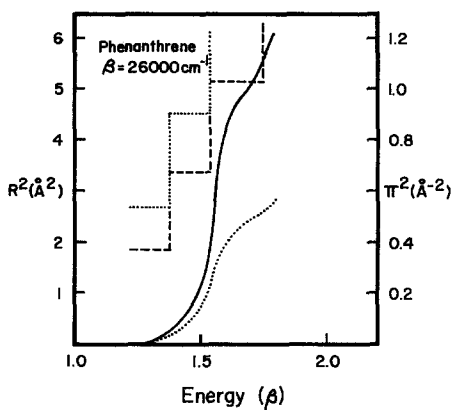


Fig. 2d

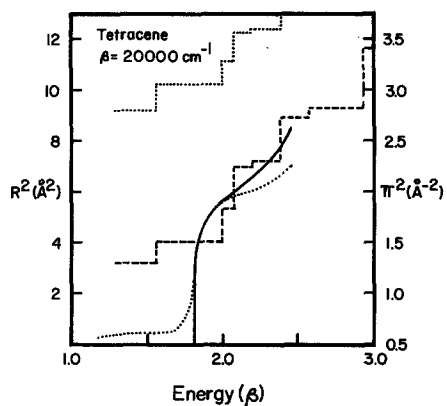


Fig. 2e

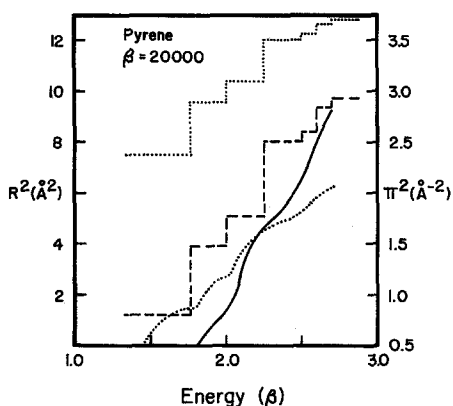


Fig. 2f

Fig. 2a-h. Cumulative absorption cross section as a function of Hückel promotion energies. —  $\Pi^2$  (expt.), - - -  $\Pi^2$  (theor.), ···· lower line  $R^2$  (expt.), ···· upper line  $R^2$  (theor.)

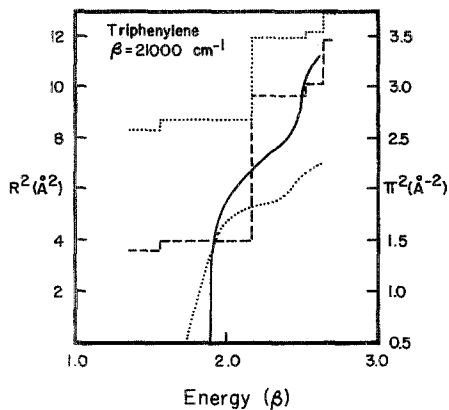


Fig. 2g

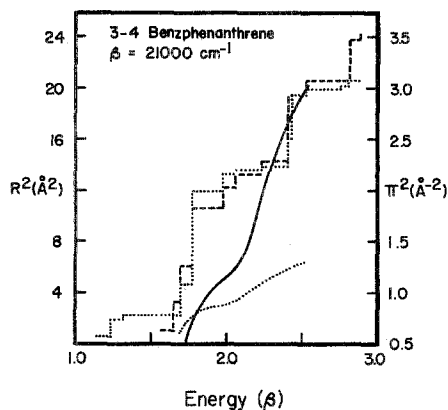


Fig. 2h

is asymptotically invariant to any degree of CI among the singly-excited states. Intensity is merely reshuffled among the transitions.

One effect might invalidate even this comparison of gross spectral cross-sections: doubly excited configurations introduced by electron correlation would not preserve the integrated intensity. In this connection it is hardly necessary to point out that the main users of  $\pi$ -electron wavefunctions for large aromatic molecules do not generally include such terms, so the comparison rests on a practical basis.

### Discussion

For exact wave functions  $f_1$  and  $f_2$  must be equal and in agreement with experimental  $f$  values. However, for quite good wavefunctions, there can be considerable disagreement among  $f_1$ ,  $f_2$ , and  $f_{\text{exp}}$ . Thus in recent publications Rothenberg and Davidson [14] found considerable divergence for  $\text{H}_2$  while Huo [15] has found erratic results in NH and CH. These are studies based on far more accurate functions than those considered in the present paper. Thus whether either  $f_1$  or  $f_2$  will be good for estimating intensity does not, at present, appear to be understood. We have therefore posed the question in somewhat limited terms: given a  $\pi$ -electron aromatic system and transitions from a closed shell ground state, which operator gives values consistent with experiment. The answer is unambiguous that  $f_2$  is the operator of choice. Since various calculations have shown that inclusion of doubly excited states bring  $f_1$  closer to experiment, the failure of  $f_1$  must relate to configuration interaction. But just how is not clear.

Our present studies are sufficiently accurate to add weight to the choice of the more modern experimental oscillator strengths over the older values of Platt and Kleven. Further, our results suggest that no discussion of intensities of  $\pi$ -electron systems should be carried out without reference to both  $f_1$  and  $f_2$ , with the latter more likely to give agreement with the data in the absence of configuration interaction with doubly excited states. The reason for the failure of  $f_1$  and the success of  $f_2$  needs further theoretical investigation.



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## Appendix

### *Effect of Refractive Index on Oscillator Strengths*

A subdued, but long-standing, debate [16] continues on the question of whether systematic differences exist between solution and vapor oscillator strengths. The consensus of modern opinion [17] appears to favor the idea that intensity is little affected by the medium and that the correction is due to the "effective field" experienced by the absorbing molecule.

Thus

$$\frac{f_{\text{liq}}}{f_{\text{gas}}} = \frac{1}{n} \left( \frac{n^2 + 2}{3} \right)^2.$$

For  $n = 1 + \delta$ ,

$$f_{\text{liq}} \approx (1 + 0.33 \delta) f_{\text{gas}}$$

and the correction should be of order 10–20 per cent for common solvents. No experimental study has ever validated the above equations for electronic transitions so we felt justified in comparing our calculations with solution spectra uncorrected for the refractive index factor. Although Ferguson *et al.* [10] report a serious solution-vapor discrepancy, in later unpublished work the solution-vapor intensities were shown to be in better agreement. No conclusion could be reached regarding the refractive index factor because of the magnitude of the experimental error.

Bakhshiev [18] has recently discussed the effective field correction and also suggested that the discrepancy between  $f_1$  and experiment is due to this factor which is close to 1 and a factor of 3 mistakenly omitted from the relation (9) between  $f$  and the molar absorption coefficient. The latter factor is asserted to be necessary in order to take "account of the random orientations of the absorbing oscillators with respect to the field of the light wave." He then corrects the discrepancy by multiplying the experimental values by the effective field correction and the factor of 3. However, it appears to us that from his arguments the theoretical values should also be multiplied by 3 and so the problem of the discrepancy remains unresolved.

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