THE ABSORPTION AND THE EMISSION SPECTRA OF SOME SUBSTITUTED 3-PHENYLCOUMARINS†

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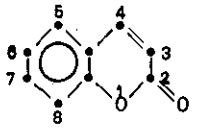
Additive substituent rules are described which correlate the absorption and the emission maxima, λ_{max} and E_{max}, of 3-phenylcoumarins substituted at 7- and 4'-positions. For these compounds, the correlation between transition energies calculated from simple Hückel Molecular Orbital (HMO) treatment and the observed E_{max} values is better than that for the observed λ_{max} values.

Coumarins (I), either naturally occurring or man-made, are highly fluorescent materials and have been widely used as optical

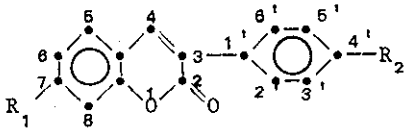


(I)

† Dedicated to Professor R. B. Woodward on his 60th birthday.

brighteners[1a] especially for wool, synthetic fabrics, and plastics. Lately, this class of compounds has also shown some promise as laser dyes.[1b]

We are, therefore, interested in correlating the spectral properties of these compounds with structural variations. Here we present evidence that both the absorption and the emission maxima (λ_{max} and E_{max}) of 7- and/or 4'-substituted 3-phenylcoumarins (II) can be correlated by means of simple, additive



(II)

substituent rules, and these empirical rules can be used to predict the λ_{max} and E_{max} of a given compound of this class within experimental error.

The observed λ_{max} and E_{max} values[2] in ethanol for some monosubstituted 3-phenylcoumarins (II) are given in Table I.

Table I. The λ_{max} and E_{max} Values (in nm) of Some Monosubstituted 3-Phenylcoumarins (II) in Ethanol

For R_2 = H

Compound No. (Fig. 1 and 2)	R_1	λ_{max} (nm)	E_{max} (nm)
1	H	325	417
2	OH	342	432
3	OCH_3	338	425
4	OCOR (R = alkyl or aryl)	331	424
5	NH_2	380	460
6	$NHCOCH_3$	344	440

For R_1 = H

	R_2	λ_{max} (nm)	E_{max} (nm)
7	OH	341	460
8	OCH_3	337	440
9	$OCOCH_3$	329	420
10	NH_2	360	no fluorescence
11	$NHCOCH_3$	337	455
12	Cl	327	420

The substituent constants ($\Delta\lambda_{max}$ and ΔE_{max}), defined as follows for the monosubstituted compounds,

$$\lambda_{max}\ (\text{sub.}) = 325\ \text{nm} + \Delta\lambda_{max}\ (\text{sub.}) \qquad (1)$$

$$E_{max}\ (sub.) = 417\ nm + \Delta E_{max}\ (sub.) \qquad (2)$$

are given in Table II.

Table II. The Substituent Constants, $\Delta\lambda_{max}$ and ΔE_{max} (in nm) of Some Monosubstituted 3-Phenylcoumarins (II) in Ethanol

For 7-Substituents

Compound No. (Fig. 1 and 2)	R_1	$\Delta\lambda_{max}$ (nm)	ΔE_{max} (nm)
1	H	0	0
2	OH	17	15
3	OCH_3	13	8
4	OCOR (R = alkyl or aryl)	6	7
5	NH_2	55	43
6	$NHCOCH_3$	19	23

For 4'-Substituents

	R_2	$\Delta\lambda_{max}$ (nm)	ΔE_{max} (nm)
7	OH	16	43
8	OCH_3	12	23
9	$OCOCH_3$	4	3
10	NH_2	35	no fluorescence
11	$NHCOCH_3$	12	38
12	Cl	2	3

If the substituent effects are indeed additive, then we have for 7- and 4'-disubstituted 3-phenylcoumarins (II)

$$\lambda_{max} = 325 + \sum \Delta\lambda_{max} \text{ (nm)} \quad (3)$$

and

$$E_{max} = 417 + \sum \Delta E_{max} \text{ (nm)} \quad (4)$$

where $\Delta\lambda_{max}$ and ΔE_{max} are the substituent constants defined by equations (1) and (2) and given in Table II and the summation is over both 7- and 4'-positions. Table III gives the differences between λ_{max} and E_{max} for calculated and observed values for seventeen 7- and 4'-disubstituted 3-phenylcoumarins (II).

Table III. Differences in Calculated and Observed λ_{max} and E_{max} for 14 Disubstituted 3-Phenylcoumarins in Ethanol

Compound No. (Fig. 1 and 2)	R_1	R_2	Difference[a] (in nm) λ_{max}	E_{max}
23	CH_3COO	$NHCOCH_3$	-1	+3
13	HO	Cl	+1	+5
14	CH_3O	Cl	+3	+7
15	CH_3COO	Cl	-1	+3
16	HO	OH	-4	-5
17	HO	OCH_3	-4	+5
18	CH_3O	OCH_3	-4	+2
19	CH_3COO	OCH_3	-3	+3
20	CH_3COO	$OCOCH_3$	-1	+8
21	HO	NH_2	-10	--[b]
22	CH_3O	NH_2	-8	--[b]
24	C_6H_5COO	$NHCOC_6H_5$	-2	-7
25	CH_3O	$NHCOCH_3$	-2	-3
26	CH_3O	$NHCOC_6H_5$	-2	-8

Apart from compounds 21 and 22,[3] there is a good agreement between observed and calculated λ_{max} and E_{max} values, and in most cases the deviations are less than twice that of our precision of measurement. Such additive substituent effects

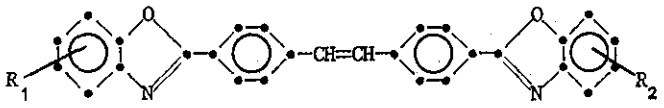
[a]Defined as observed - calculated.

[b]No fluorescence from these two compounds.

in λ_{max} are not entirely unexpected. For example, the Woodward additivity rules for diene absorption[4] are well-known and have proven to be invaluable in the study of the uv spectra of dienes and steroids; also, studies of a number of disubstituted acetophenones[5] showed that additivity apparently is not limited to dienes. Since fluorescence spectra usually exhibit a mirror-image relationship[6] to absorption spectra, additivity in E_{max} should also be anticipated provided that the differences in Stokes shifts are small for compounds under consideration. Nevertheless, we believe that this is the first time such an additivity in E_{max} has been treated explicitly.

Although correlation between observed spectral data and calculated Hückel transition energies cannot be regarded as a quantum chemical justification of the additivity rules, we have correlated observed λ_{max} and E_{max} values for 26 mono- or disubstituted 3-phenylcoumarins (II) with transition energies obtained from Hückel Molecular Orbital (HMO) calculations.[7] As can be seen from Figure 1, the correlation between λ_{max} and calculated Hückel transition energies is only fair (correlation coefficient = 0.71 and standard deviation = 747.60 cm^{-1}). When the E_{max} values are plotted in the same manner, good correlation is obtained (correlation coefficient = 0.90, standard deviation = 371.18 cm^{-1}). We have no explanation for the better correlation with E_{max} than λ_{max}. We also measured (in carbon tetrachloride) the λ_{max} and the E_{max} of 16 of the 26 compounds listed in Figures 1 and 2 (selection of the compounds was based on solubility in CCl_4) and again correlated them with the calculated Hückel transition energies. The results are given in Figures 3

and 4. The correlation is once again not as good with λ_{max} (correlation coefficient = 0.563 and standard deviation = 586.49 cm^{-1}) as with E_{max} (correlation coefficient = 0.6454 and standard deviation = 417.07 cm^{-1}). For the same set of compounds with λ_{max} and E_{max} measured in EtOH (part of the data from Figs. 1 and 2), correlation coefficient = 0.495 and standard deviation = 844.35 cm^{-1} for correlation with λ_{max}, and correlation coefficient = 0.866 and standard deviation = 394.47 cm^{-1} with E_{max}. Despite the fact that the good correlation with E_{max} in EtOH (correlation coefficient = 0.90 with standard deviation = 371.18 cm^{-1}) enables us to predict[8] E_{max} for this particular series of compounds to within $\pm$5 nm (experimental error) with at least 90% confidence, we think such a correlation may be simply fortuitous. We have also found that even though additivity rules (with a different set of substituent constants than those given in Table II) apply[9] to substituted bis-benzoxazoylstilbenes (III), another class of important optical brighteners, the correlations obtained from 3-phenylcoumarins cannot be applied there.



(III)

ACKNOWLEDGEMENT We thank L. Costa for measuring all the absorption and the emission data reported here.

Figure 1. Correlation between λ_{max} (in wavenumbers) observed in EtOH and Hückel transition energy calculated.

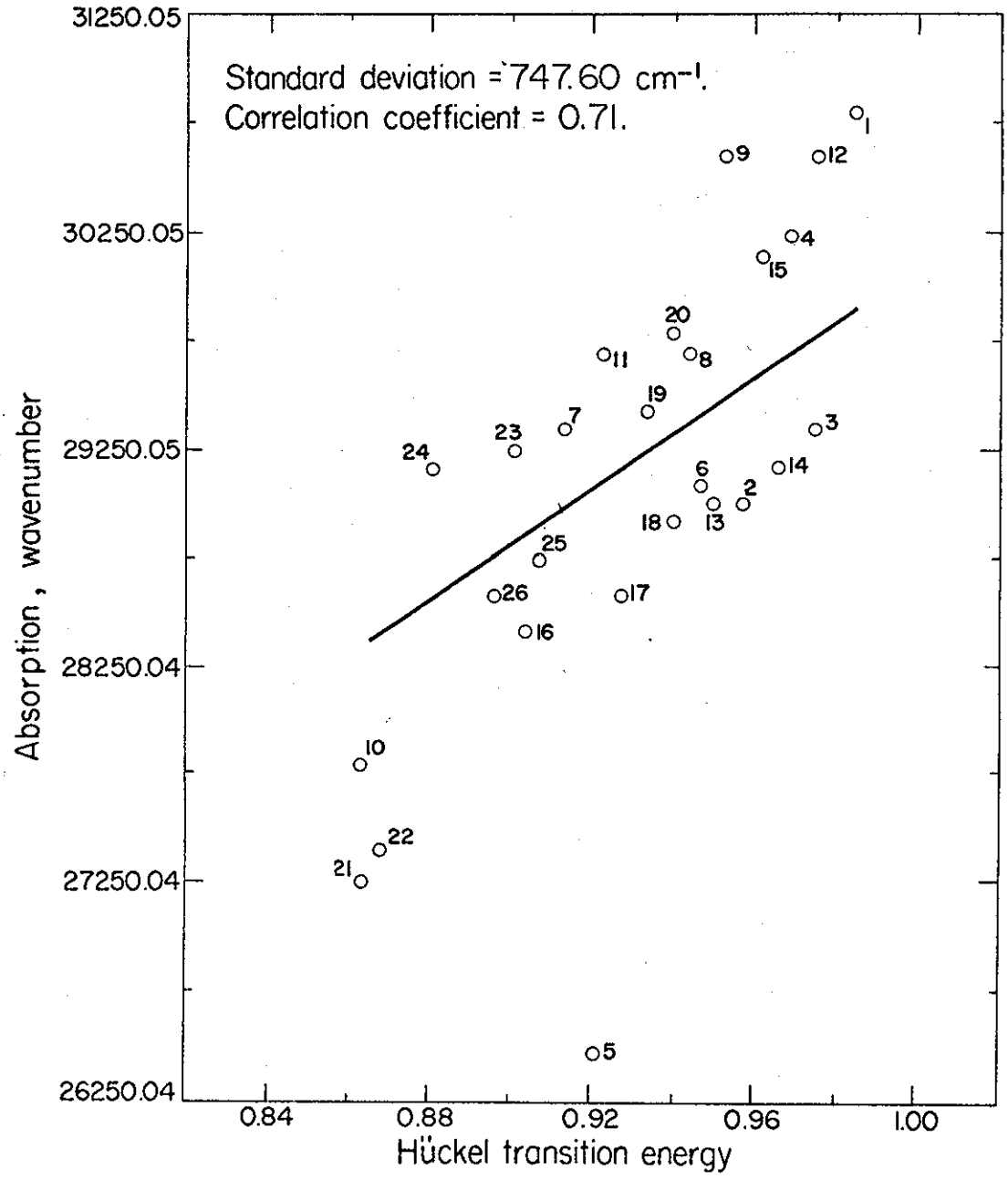


Figure 2. Correlation between E_{max} observed in EtOH and Hückel transition energy calculated.

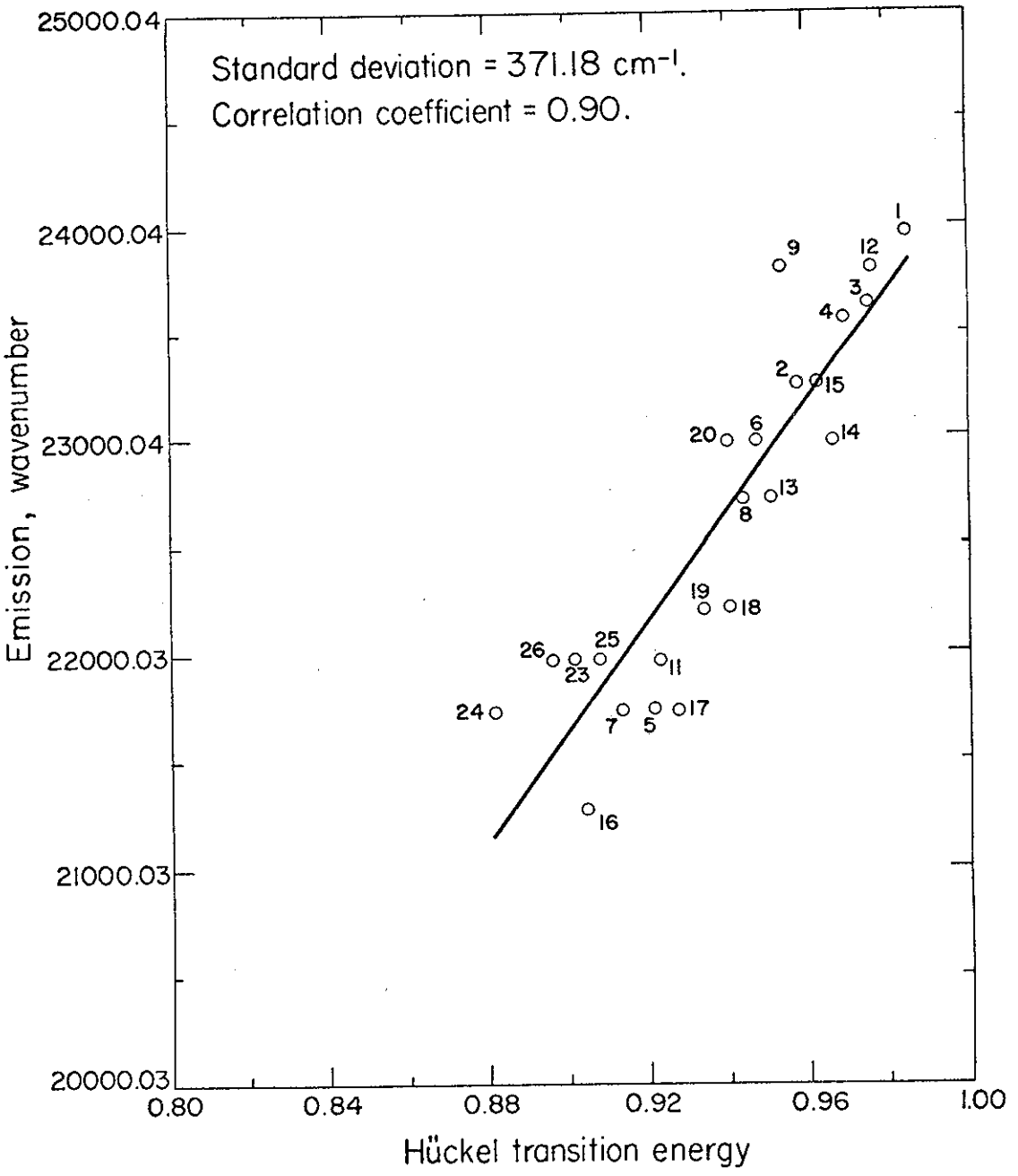
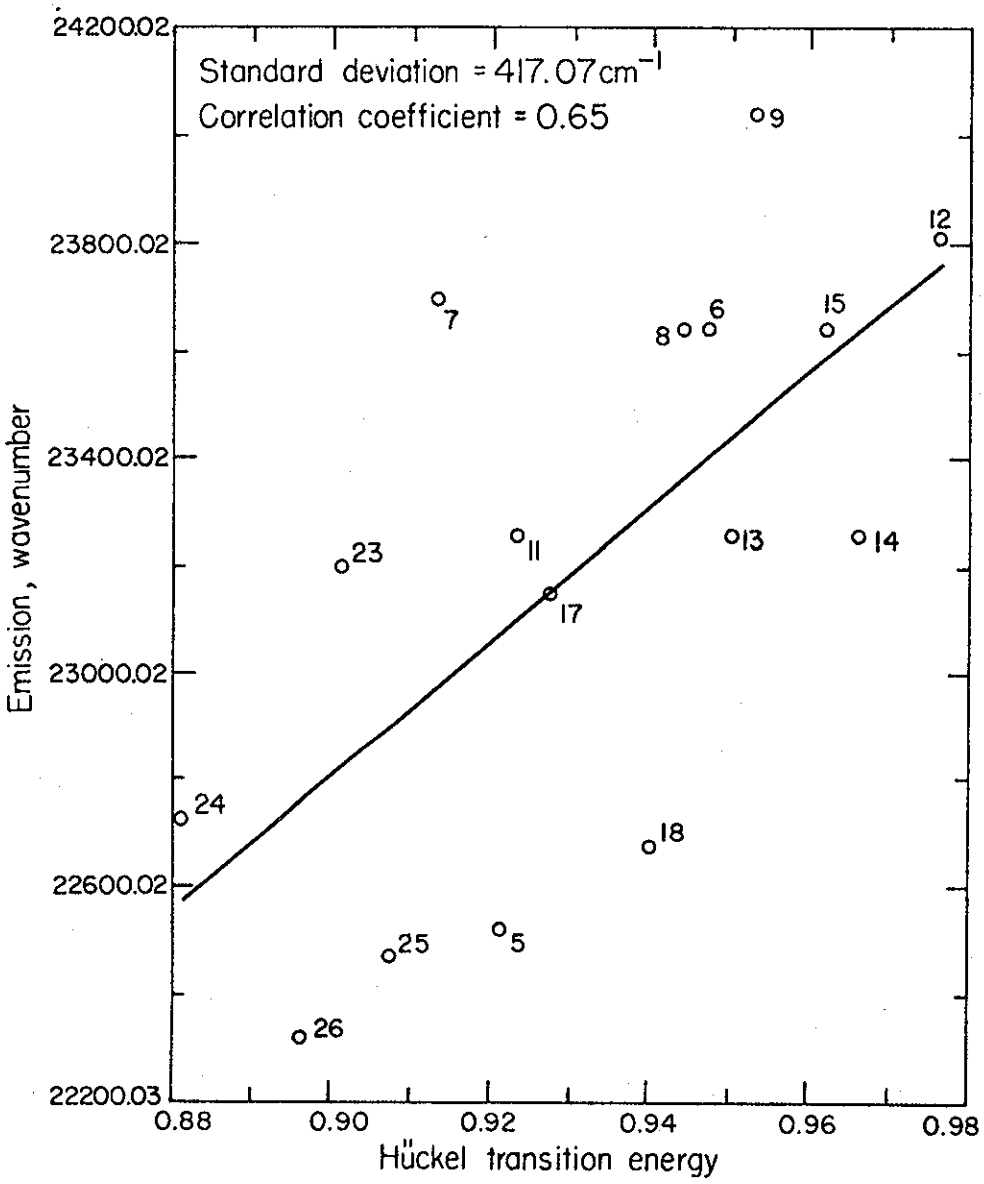


FIGURE 3


Standard deviation = 417.07cm⁻¹
Correlation coefficient = 0.65
Emission, wavenumber
Hückel transition energy
24200.02
23800.02
23400.02
23000.02
22600.02
22200.03
0.88
0.90
0.92
0.94
0.96
0.98
9
12
7
6
8
15
23
11
13
14
17
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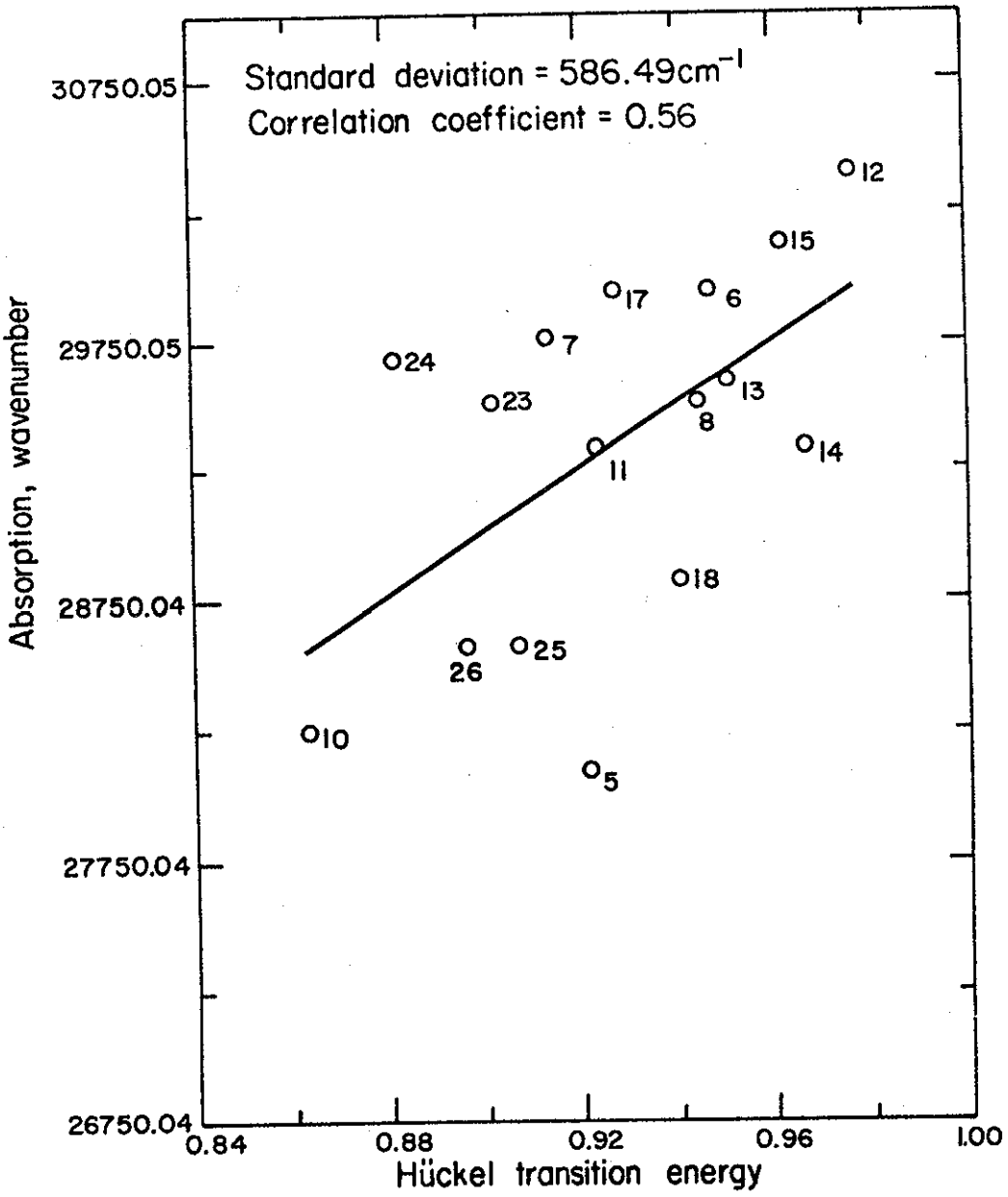
5
26

FIGURE 4


Standard deviation = 586.49cm⁻¹
Correlation coefficient = 0.56
30750.05
29750.05
28750.04
27750.04
26750.04
Absorption, wavenumber
0.84
0.88
0.92
0.96
1.00
Hückel transition energy
12
15
17
6
7
24
13
23
8
14
11
18
25
26
10
5

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2 Absorption spectra were recorded with a Cary 14 spectrometer. The solutions used had concentrations of 10^{-4} and 10^{-5} M. Within this range, the λ_{max} and E_{max} recorded were independent of the concentration. Emission spectra were measured with an instrument described by Costa et al. [L. Costa, F. Grum, and D. J. Paine, Appl. Opt., 1969, 8, 1149]. The precision of measurement is ±5 nm for E_{max} and ±3 nm for λ_{max}.

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Received, 28th September, 1977