

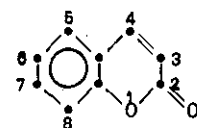
THE ABSORPTION AND THE EMISSION SPECTRA OF SOME  
 SUBSTITUTED 3-PHENYLCOUMARINS<sup>†</sup>

C. Y. Chen\* and T. E. Gompf

Research Laboratories, Eastman Kodak Company, Rochester, New York  
14650, U.S.A.

Additive substituent rules are described which correlate the absorption and the emission maxima,  $\lambda_{\max}$  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  $\lambda_{\max}$  values.

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

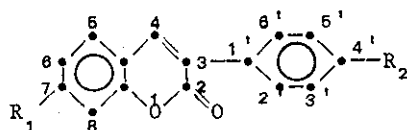


(I)

<sup>†</sup> Dedicated to Professor R. B. Woodward on his 60th birthday.

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

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 ( $\lambda_{\max}$  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  $\lambda_{\max}$  and  $E_{\max}$  of a given compound of this class within experimental error.

The observed  $\lambda_{\max}$  and  $E_{\max}$  values<sup>2</sup> in ethanol for some monosubstituted 3-phenylcoumarins (II) are given in Table I.

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

<u>For <math>R_2 = H</math></u>			
<u>Compound No.</u> (Fig. 1 and 2)	<u><math>R_1</math></u>	<u><math>\lambda_{\max}</math> (nm)</u>	<u><math>E_{\max}</math> (nm)</u>
1	H	325	417
2	OH	342	432
3	OCH <sub>3</sub>	338	425
4	OCOR (R = alkyl or aryl)	331	424
5	NH <sub>2</sub>	380	460
6	NHCOCH <sub>3</sub>	344	440
<u>For <math>R_1 = H</math></u>			
	<u><math>R_2</math></u>	<u><math>\lambda_{\max}</math> (nm)</u>	<u><math>E_{\max}</math> (nm)</u>
7	OH	341	460
8	OCH <sub>3</sub>	337	440
9	OCOCH <sub>3</sub>	329	420
10	NH <sub>2</sub>	360	no fluorescence
11	NHCOCH <sub>3</sub>	337	455
12	Cl	327	420

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

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

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

are given in Table II.

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

For 7-Substituents

<u>Compound No.</u> (Fig. 1 and 2)	<u>R<sub>1</sub></u>	<u><math>\Delta\lambda_{\max}</math> (nm)</u>	<u><math>\Delta E_{\max}</math> (nm)</u>
1	H	0	0
2	OH	17	15
3	OCH <sub>3</sub>	13	8
4	OCOR (R = alkyl or aryl)	6	7
5	NH <sub>2</sub>	55	43
6	NHCOCH <sub>3</sub>	19	23

For 4'-Substituents

	<u>R<sub>2</sub></u>	<u><math>\Delta\lambda_{\max}</math> (nm)</u>	<u><math>\Delta E_{\max}</math> (nm)</u>
7	OH	16	43
8	OCH <sub>3</sub>	12	23
9	OCOCH <sub>3</sub>	4	3
10	NH <sub>2</sub>	35	no fluorescence
11	NHCOCH <sub>3</sub>	12	38
12	Cl	2	3

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

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

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

where  $\Delta\lambda_{\max}$  and  $\Delta E_{\max}$  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  $\lambda_{\max}$  and  $E_{\max}$  for calculated and observed values for seventeen 7- and 4'-disubstituted 3-phenylcoumarins (II).

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

Compound No. (Fig. 1 and 2)	$R_1$	$R_2$	Difference <sup>a</sup> (in nm)	
			$\lambda_{\max}$	$E_{\max}$
23	CH <sub>3</sub> COO	NHCOCH <sub>3</sub>	-1	+3
13	HO	Cl	+1	+5
14	CH <sub>3</sub> O	Cl	+3	+7
15	CH <sub>3</sub> COO	Cl	-1	+3
16	HO	OH	-4	-5
17	HO	OCH <sub>3</sub>	-4	+5
18	CH <sub>3</sub> O	OCH <sub>3</sub>	-4	+2
19	CH <sub>3</sub> COO	OCH <sub>3</sub>	-3	+3
20	CH <sub>3</sub> COO	OCOCH <sub>3</sub>	-1	+8
21	HO	NH <sub>2</sub>	-10	-- <sup>b</sup>
22	CH <sub>3</sub> O	NH <sub>2</sub>	-8	-- <sup>b</sup>
24	C <sub>6</sub> H <sub>5</sub> COO	NHCOC <sub>6</sub> H <sub>5</sub>	-2	-7
25	CH <sub>3</sub> O	NHCOCH <sub>3</sub>	-2	-3
26	CH <sub>3</sub> O	NHCOC <sub>6</sub> H <sub>5</sub>	-2	-8

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

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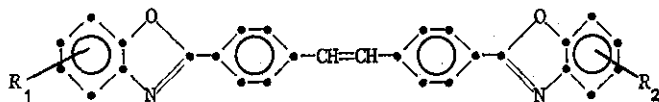
<sup>a</sup>Defined as observed - calculated.

<sup>b</sup>No fluorescence from these two compounds.

in  $\lambda_{\max}$  are not entirely unexpected. For example, the Woodward additivity rules for diene absorption<sup>4</sup> 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<sup>5</sup> showed that additivity apparently is not limited to dienes. Since fluorescence spectra usually exhibit a mirror-image relationship<sup>6</sup> 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  $\lambda_{\max}$  and  $E_{\max}$  values for 26 mono- or disubstituted 3-phenylcoumarins (II) with transition energies obtained from Hückel Molecular Orbital (HMO) calculations.<sup>7</sup> As can be seen from Figure 1, the correlation between  $\lambda_{\max}$  and calculated Hückel transition energies is only fair (correlation coefficient = 0.71 and standard deviation = 747.60  $\text{cm}^{-1}$ ). When the  $E_{\max}$  values are plotted in the same manner, good correlation is obtained (correlation coefficient = 0.90, standard deviation = 371.18  $\text{cm}^{-1}$ ). We have no explanation for the better correlation with  $E_{\max}$  than  $\lambda_{\max}$ . We also measured (in carbon tetrachloride) the  $\lambda_{\max}$  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  $\text{CCl}_4$ ) 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  $\lambda_{\max}$  (correlation coefficient = 0.563 and standard deviation = 586.49  $\text{cm}^{-1}$ ) as with  $E_{\max}$  (correlation coefficient = 0.6454 and standard deviation = 417.07  $\text{cm}^{-1}$ ). For the same set of compounds with  $\lambda_{\max}$  and  $E_{\max}$  measured in EtOH (part of the data from Figs. 1 and 2), correlation coefficient = 0.495 and standard deviation = 844.35  $\text{cm}^{-1}$  for correlation with  $\lambda_{\max}$ , and correlation coefficient = 0.866 and standard deviation = 394.47  $\text{cm}^{-1}$  with  $E_{\max}$ . Despite the fact that the good correlation with  $E_{\max}$  in EtOH (correlation coefficient = 0.90 with standard deviation = 371.18  $\text{cm}^{-1}$ ) enables us to predict<sup>8</sup>  $E_{\max}$  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<sup>9</sup> to substituted bis-benzoxazolylstilbenes (III), another class of important optical brighteners, the correlations obtained from 3-phenylcoumarins cannot be applied there.



(III)

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

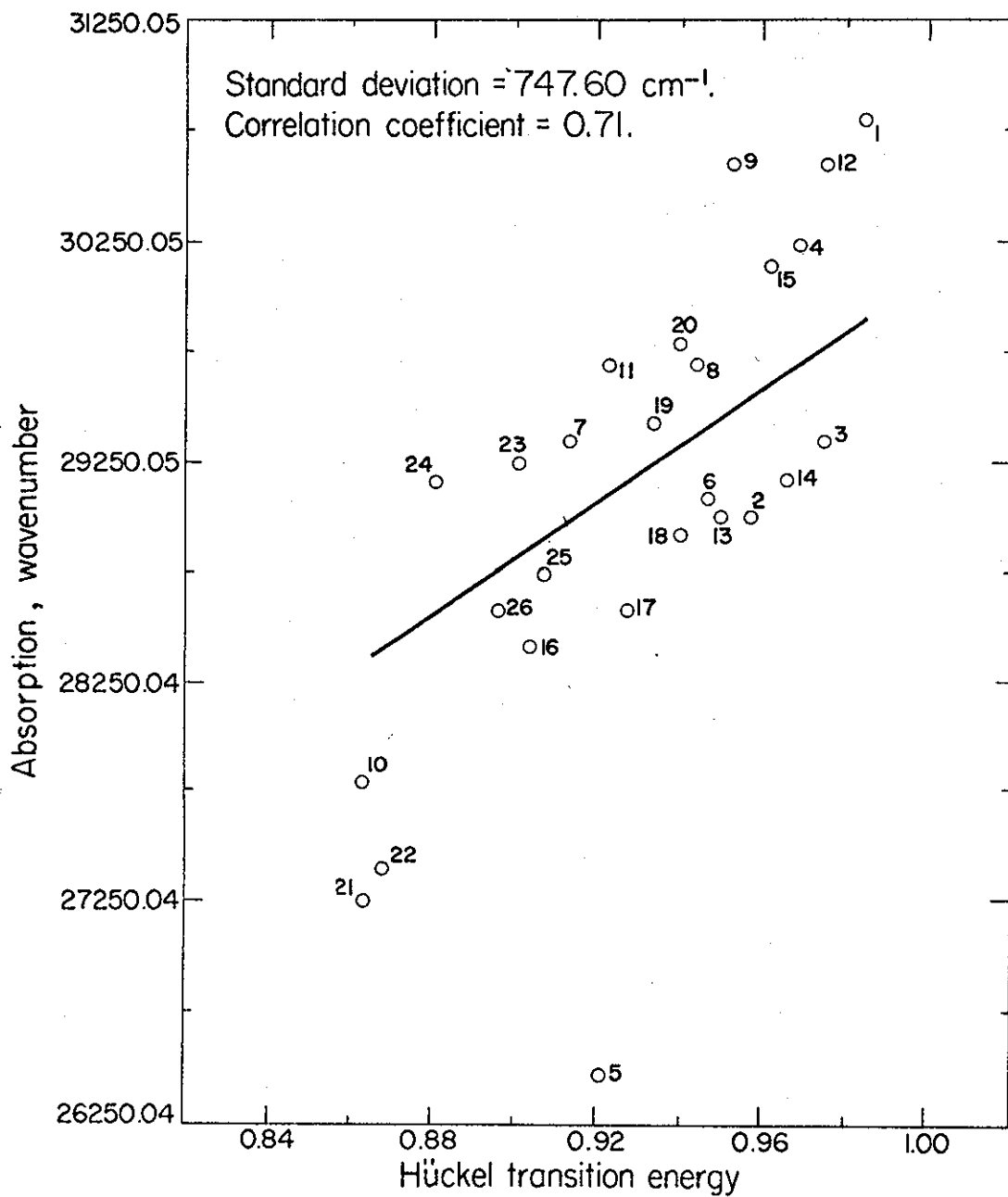


Figure 2. Correlation between  $E_{\max}$  observed in EtOH and Hückel transition energy calculated.

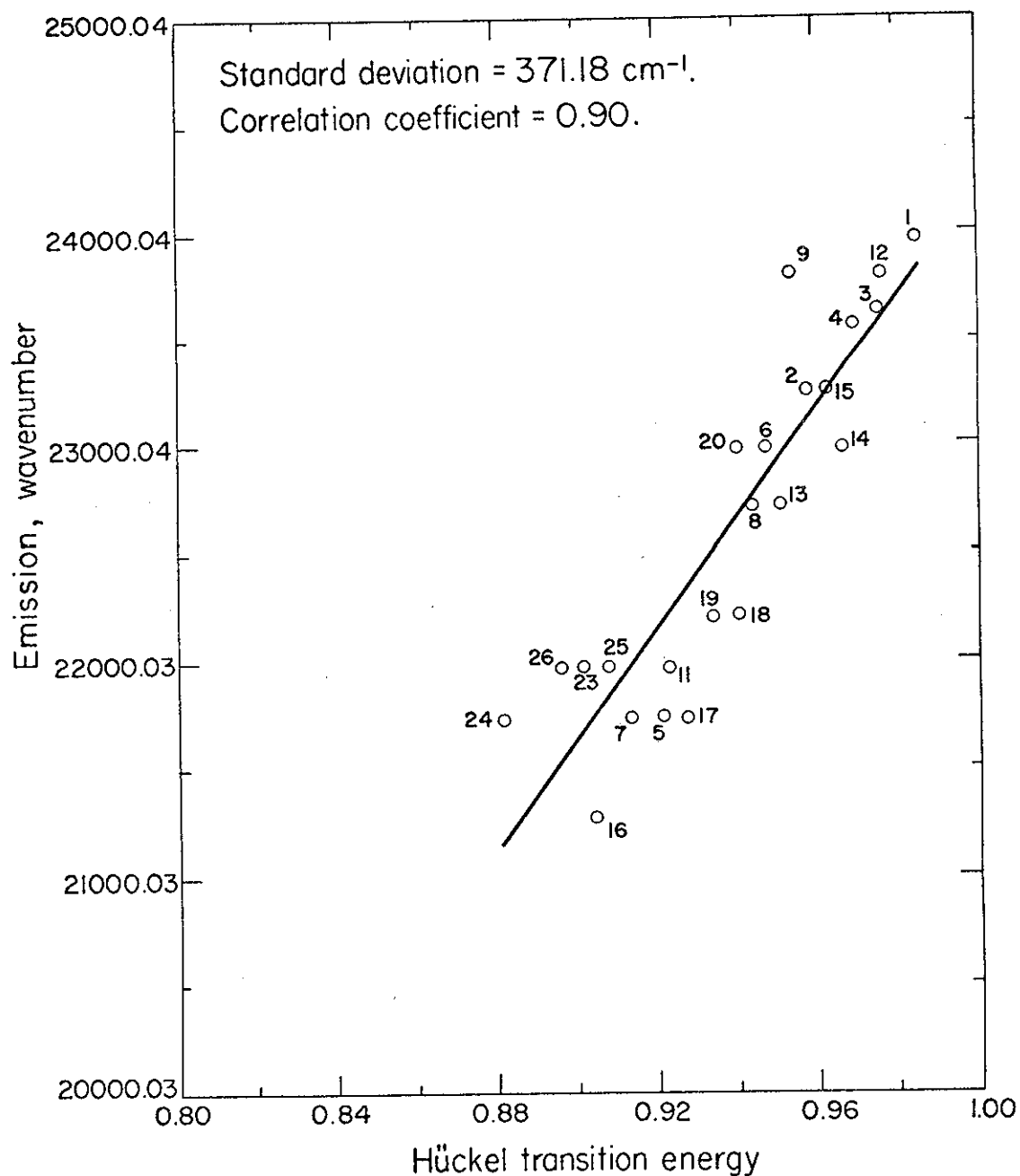


FIGURE 3

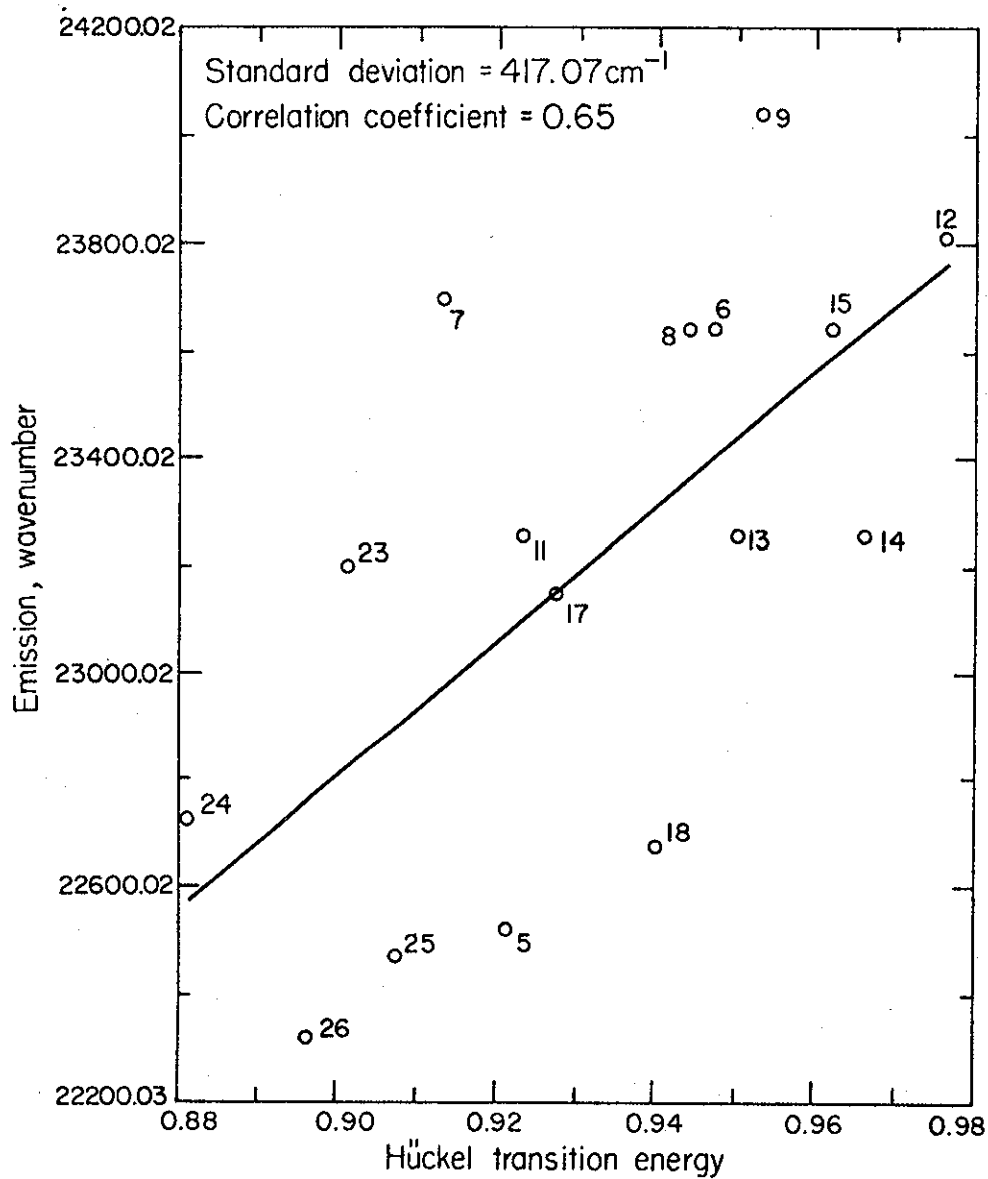
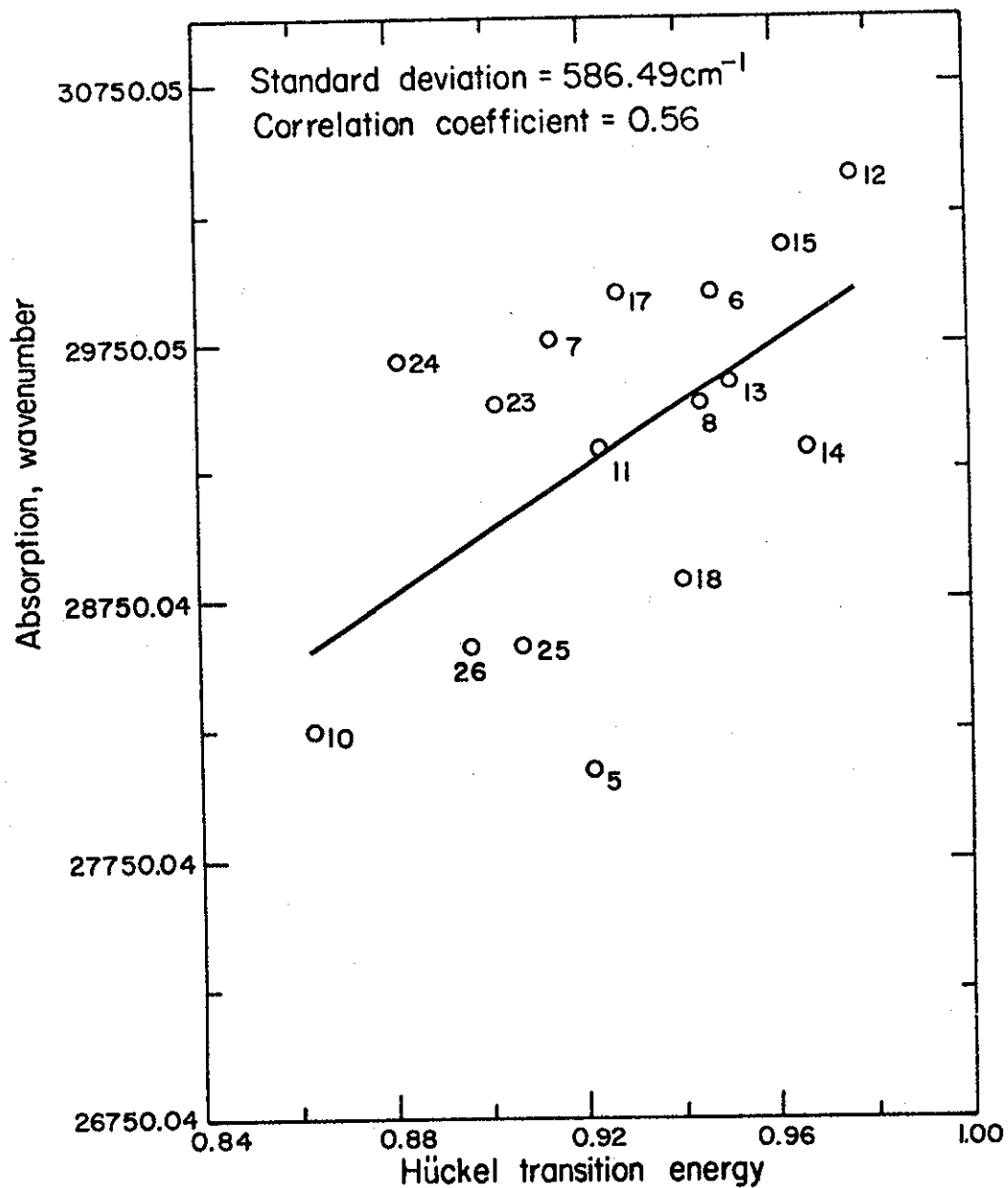


FIGURE 4



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