Supplementary Information (SI) for New Journal of Chemistry.

Analyzing Experimental UV-Vis Spectra of Conjugated Molecules in Solution: Pekarian Function Fit

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$$PF(\nu) = e^{-S_1-S_2}\sum_{k_1=0}^{\infty}\frac{S_1^{k_1}}{k_1!}\left[\sum_{k_2=0}^{\infty}\frac{S_2^{k_2}}{k_2!}G(1,\nu_0 \pm k_1\Omega_1 \pm k_2\Omega_2,\sigma_0\right] \quad (1S)$$

This approximation can be used in the case when two different Ω are visible (spectra recorded in the gas phase, for instance). The signs '+' are for absorption and '-' for fluorescence. Generalization of P(ν) for any number of vibrational modes is also possible.

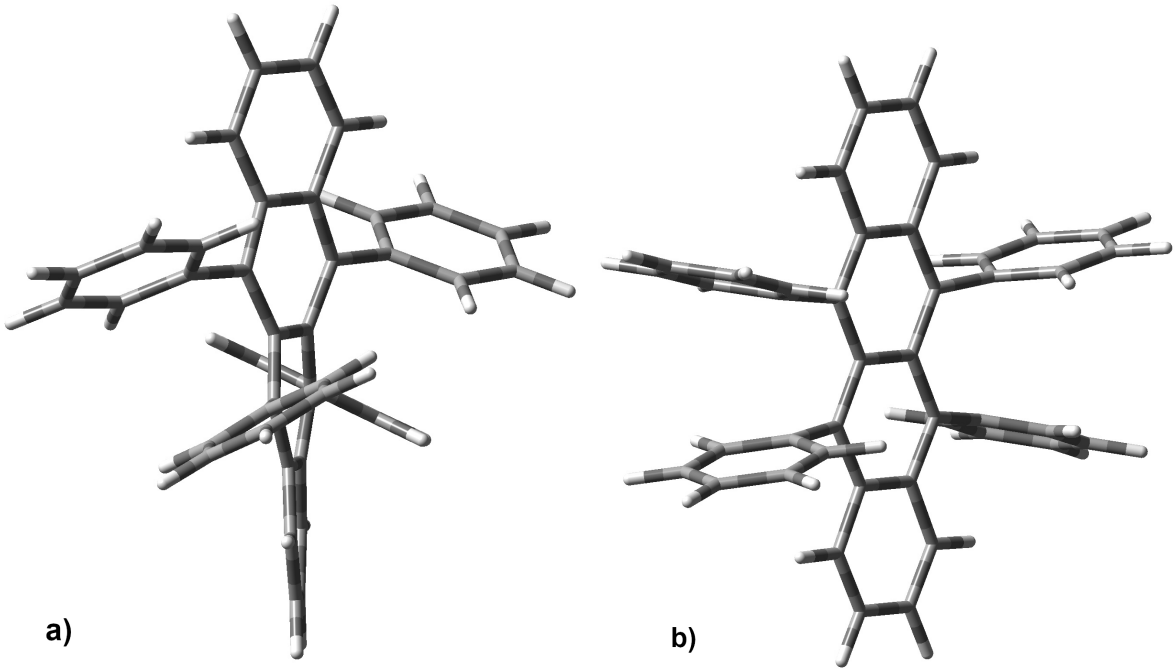

Figure 1S. Rubrene frequency calculation result: B3LYP/Aug-CC-pVDZ; temperature 298.15 K.

a) GS, Imaginary freq = 0; point group = D2; electronic energy (EE) = -1617.5046 Hartree; EE + thermal free energy correction = -1617.0076 Hartree.

b) TS, Imaginary freq = 1; point group = D2; electronic energy (EE) = -1617.4943 Hartree; EE + thermal free energy correction = -1616.9963 Hartree.

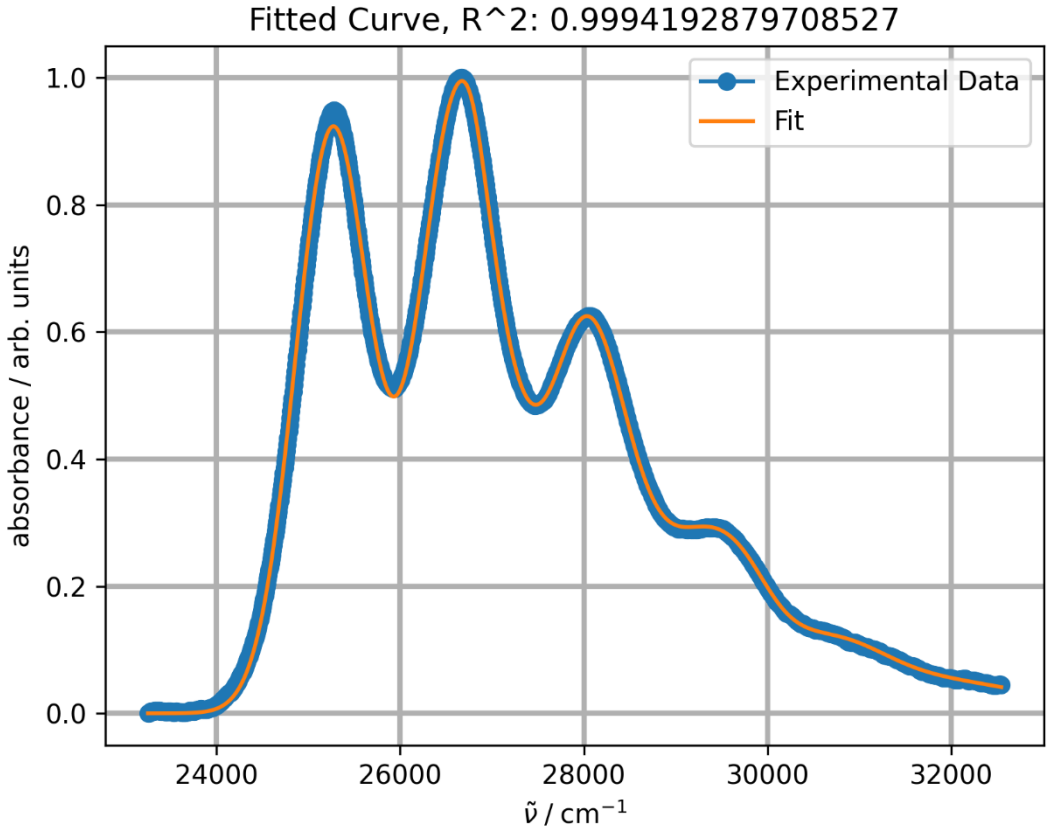

Figure 2S. Fitting results using three PF for DPA absorption spectrum in octane at 20°C

Example of the PekarFit output.

S (A0)	v_0 (A1) cm^{-1}	Ω (A2) cm^{-1}	σ_0 (A3)	δ (A4)	A5[a]

[a] normalization coefficient

PekarFit_18: DATA SUMMARY DPA Octane RT

R-squared: 0.9994192879708527

RMSE: 0.22604244649959926

AbsMax1, nm: 375.34964242904147

AbsMax2, nm: 351.6062022388348

Area_1 (%): 88.22710401196643

Area_2 (%): 8.324268575951995

Area_3 (%): 2.6955703286836394

A0: 1.0063265180120915

A1: 25258.06733240906

A2: 1375.059693314594

A3: 406.51483530648284

A4: 29.64909110156226

A5: 9.842987203247978e-05

A6: 3.8645722280515384

A7: 26205.32691145041

A8: 578.4811233331503

A9: 0.20604971038950734

A10: 110.51327422603545

A11: 2.2506162671329346e-07

A12: 1.2985893781146998

A13: 29788.14213341122

A14: 1223.4129786167905

A15: 261.07888573991653

A16: 629.6054666867499

A17: 6.150805629471176e-07

StdDev A0: 0.0016702871861527526

StdDev A1: 0.596807471572824

StdDev A2: 0.7349339018753287

StdDev A3: 0.5602849500314602

StdDev A4: 0.7443835640207691

StdDev A5: 1.7244708423672133e-07

StdDev A6: 0.062224287302376516

StdDev A7: 17.679579864738315

StdDev A8: 10.983798179475572

StdDev A9: 7.6257131632058295

StdDev A10: 4.043680443465353

StdDev A11: 1.9416727567483262e-08

StdDev A12: 0.0793896214582211

StdDev A13: 29.075938372839598

StdDev A14: 75.12474159105207

StdDev A15: 40.24725942560572

StdDev A16: 124.89200281726144

StdDev A17: 8.131367062382272e-08

Origin Absorption FDF

[General Information]

Function Name = Pek9

Brief Description =

Function Source = N/A

Number Of Parameters = 7

Function Type = User-Defined

Function Form = Equations

Path =

Number Of Independent Variables = 1

Number Of Dependent Variables = 1

Function Model = Explicit

[Fitting Parameters]

Names = y0,A0,A1,A2,A3,A4,A5

Initial Values = 25400(V),1(V),25400(V),1390(V),370(V),50(V),0.1(V)

Meanings = ?,?,?,?,?,?,?

Lower Bounds = 12000(I, On),0.2(I, On),12000(I, On),100(I, On),10(I, On),10(I, On),0(I, On)

Upper Bounds = 40000(I, On),8(I, On),40000(I, On),2000(I, On),1000(I, On),1000(I, On),1(I, On)

Naming Method = User-Defined

Number Of Significant Digits = 0,0,0,0,0,0,0

Unit = ,,,,,,

Format = --,--,--,--,--,--,--

CustomDisplay = --,--,--,--,--,--,--

[Independent Variables]

x =

[Dependent Variables]

y =

[Formula]

y0 = A1

F1=nlf_gaussa(x,0,A1,A3,1)

F2=A0*nlf_gaussa(x,0,A1+A2,A3+A4,1)

F3=(A0^2/2)*nlf_gaussa(x,0,A1+2*A2,A3+2*A4,1)

F4=(A0^3/6)*nlf_gaussa(x,0,A1+3*A2,A3+3*A4,1)

F5=(A0^4/24)*nlf_gaussa(x,0,A1+4*A2,A3+4*A4,1)

F6=(A0^5/120)*nlf_gaussa(x,0,A1+5*A2,A3+5*A4,1)

F7=(A0^6/720)*nlf_gaussa(x,0,A1+6*A2,A3+6*A4,1)

F8=(A0^7/5040)*nlf_gaussa(x,0,A1+7*A2,A3+7*A4,1)

F9=(A0^8/40320)*nlf_gaussa(x,0,A1+8*A2,A3+8*A4,1)

y=A5*x*EXP(-A0)*(F1+F2+F3+F4+F5+F6+F7+F8+F9)

[Constraints]

[Initializations]

[After Fitting]

[Constants]

[Controls]

General Linear Constraints = 0

Initialization Scripts = 0

Scripts After Fitting = 0

Number Of Duplicates = 0

Duplicate Offset = 2

Duplicate Unit = 6

Generate Curves After Fitting = 1

Curve Point Spacing = Uniform on X-Axis Scale

Generate Peaks After Fitting = 1

Generate Peaks During Fitting = 1

Generate Peaks with Baseline = 1

Paste Parameters to Plot After Fitting = 1

Paste Parameters to Notes Window After Fitting = 1

Generate Residuals After Fitting = 0

Keep Parameters = 0

Compile On Param Change Script = 0

Enable Parameters Initialization = 1

Treat All Numbers As Double = 1

Peak Center = 3

Peak Width = 5

Peak Amplitude = 2

[Compile Function]

Compile = 0

Compile Parameters Initialization = 1

OnParamChangeScriptsEnabled = 0.

[Parameters Initialization]

//Code to be executed to initialize parameters

[Origin C Function Header]

[Origin C Parameter Initialization Header]

[Derived Parameters]

F1 = nlf_gauss(x,0,A1,A3,1)

F2 = A0*nlf_gauss(x,0,A1+A2,A3+A4,1)

F3 = (A0^2/2)*nlf_gauss(x,0,A1+2*A2,A3+2*A4,1)

F4 = (A0^3/6)*nlf_gauss(x,0,A1+3*A2,A3+3*A4,1)

F5 = (A0^4/24)*nlf_gauss(x,0,A1+4*A2,A3+4*A4,1)

F6 = (A0^5/120)*nlf_gauss(x,0,A1+5*A2,A3+5*A4,1)

F7 = (A0^6/720)*nlf_gauss(x,0,A1+6*A2,A3+6*A4,1)

F8 = (A0^7/5040)*nlf_gauss(x,0,A1+7*A2,A3+7*A4,1)

F9 = (A0^8/40320)*nlf_gauss(x,0,A1+8*A2,A3+8*A4,1)

[Derived Parameter Settings]

Unit = ,,,,,,,,

Names = F1,F2,F3,F4,F5,F6,F7,F8,F9

Meanings = ,,,,,,,,

[QuickCheck]

x=25000

y0=25400

A0=1

A1=25400

A2=1390

A3=370

A4=50

A5=0.1

PeakFit Absorption UDF

---

pek9
6

10

F1=GAUSSA(1,A1,A3)

F2=A0*GAUSSA(1,A1+A2,A3+A4)

F3=(A0^2/2)*GAUSSA(1,A1+2*A2,A3+2*A4)

F4=(A0^3/6)*GAUSSA(1,A1+3*A2,A3+3*A4)

F5=(A0^4/24)*GAUSSA(1,A1+4*A2,A3+4*A4)

F6=(A0^5/120)*GAUSSA(1,A1+5*A2,A3+5*A4)

F7=(A0^6/720)*GAUSSA(1,A1+6*A2,A3+6*A4)

F8=(A0^7/5040)*GAUSSA(1,A1+7*A2,A3+7*A4)

F9=(A0^8/40320)*GAUSSA(1,A1+8*A2,A3+8*A4)

Y=A5*X*EXP(-A0)*(F1+F2+F3+F4+F5+F6+F7+F8+F9)

0 1.245 10

1E+4 25400 1E+5

100 1396 2000

50 368 1000

10 53 1000

0 0.11 1

PeakFit Fluorescence UDF

---

pek9

6

10

F1=GAUSSA(1,A1,A3)

F2=A0*GAUSSA(1,A1-A2,A3+A4)

F3=(A0^2/2)*GAUSSA(1,A1-2*A2,A3+2*A4)

F4=(A0^3/6)*GAUSSA(1,A1-3*A2,A3+3*A4)

F5=(A0^4/24)*GAUSSA(1,A1-4*A2,A3+4*A4)

F6=(A0^5/120)*GAUSSA(1,A1-5*A2,A3+5*A4)

F7=(A0^6/720)*GAUSSA(1,A1-6*A2,A3+6*A4)

F8=(A0^7/5040)*GAUSSA(1,A1-7*A2,A3+7*A4)

F9=(A0^8/40320)*GAUSSA(1,A1-8*A2,A3+8*A4)

Y=A5*X*EXP(-A0)*(F1+F2+F3+F4+F5+F6+F7+F8+F9)

0 1.245 10

1E+4 25400 1E+5

100 1396 2000

50 368 1000

10 53 1000

0 0.11 1

PeakFit fitting DPA spectrum output example (2 PF):

File Source: z:\documents\pekar\dpha\solvato\fits\hexaneen.txt

Fitted Parameters

r^2 Coef Det DF Adj r^2 Fit Std Err F-value

0.99709100 0.99705563 0.01632974 30786.1080

Peak	Type	a0	a1	a2	a3	a4	a5
1	pek8[UDF1]	1.09604722	25480.1402	1385.05239	368.160840	40.6217023	0.09471225
2	pek8[UDF1]	3.11378874	25104.9861	1231.36834	890.385825	10.0018468	0.02472527

Measured Values

Peak	Type	Amplitude	Center	FWHM	Asym50	FW Base	Asym10
1	pek8[UDF1]	0.87695878	25489.2968	2384.94849	4.46694767	6244.70081	6.04599604
2	pek8[UDF1]	0.12066590	28582.0920	5588.11143	1.19801764	11079.5498	1.39617647

Peak	Type	Anlytc Area	% Area	Int Area	% Area	Centroid	Moment2
1	pek8[UDF1]	Unknown		2553.83534	100.000000	27073.5628	2.3207e+06
2	pek8[UDF1]	Unknown		678.490646	26.5675173	28840.5649	4.2427e+06
	Total			2553.83534	100.000000		

Parameter Statistics

Peak 1 pek8[UDF1]

Parm	Value	Std Error	t-value	95	
a0	1.09604722	0.00726061	150.957972	1.08179923	1.11029521
a1	25480.1402	0.74148770	34363.5372	25478.6851	25481.5952
a2	1385.05239	1.05196027	1316.63945	1382.98806	1387.11673
a3	368.160840	1.04214842	353.271026	366.115762	370.205919
a4	40.6217023	0.88768341	45.7614752	38.8797408	42.3636637
a5	0.09471225	0.00120998	78.2760699	0.09233783	0.09708667

Peak 2 pek8[UDF1]

Parm	Value	Std Error	t-value	95

a0	3.11378874	9.03349615	0.34469365	-14.613255	20.8408322
a1	25104.9861	5478.95033	4.58207952	14353.2695	35856.7027
a2	1231.36834	1814.35955	0.67867934	-2329.0727	4791.80939
a3	890.385825	1341.35830	0.66379418	-1741.8527	3522.62438
a4	10.0018468	445.102339	0.02247089	-863.45272	883.456418
a5	0.02472527	0.00126237	19.5863782	0.02224803	0.02720250

Analysis of Variance

r^2 Coef Det	DF Adj r^2	Fit Std Err
0.99709100	0.99705563	0.01632974

Source	Sum of Squares	DF	Mean Square	F
Regr	90.303848	11	8.2094407	30786.108
Error	0.26346063	988	0.00026666056	
Total	90.567309	999		

Details of Fit

Set Convergence	State	Iterations	Minimization	Extent
1E-6	Converged	55	PVII Lim	1/1

Curvature Matrix	Constraints				Violated
Full	None	- None	- None	- None	0