

Homonuclear Two-Dimensional J-Resolved Spectroscopy. (1)
The Examination of Resonances Due to Strong Coupling in the
Two-Dimensional J-Spectrum of 1,6-Diazathianthrene: The Role of First
Order Character in the Position and Intensity of Resonances Due to
Strong Coupling

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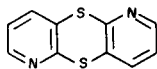
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Resonances due to strong coupling were observed in the two-dimensional J-resolved (2DJ) ^1H -nmr spectrum of 1,6-diazathianthrene. Complete analysis of the 2DJ spectral responses predicts that the resonances due to strong coupling are shifted outward from $F_1 = 0$ Hz with a corresponding diminution in intensity as the term $\nu_A - \nu_B$ increases in proceeding to successively higher spectrometer operating frequencies.

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Two-dimensional J-resolved (2DJ) homonuclear nmr experiments provide the chemist with a powerful new tool for the examination of complex nmr spectra which might otherwise be intractable at a given operating frequency. Care must, however, be exercised when strongly coupled spin systems are examined by this technique since the effects of strong coupling are manifest in the 2DJ spectra in the form of additional resonances not present in the conventional (one-dimensional) nmr spectra. Several recent studies have presented detailed expressions for the analysis of strong coupling in 2DJ spectra (3,4). Several practical demonstrations of cases of strong coupling have also been reported in the literature (5,6). A feature of these spectra which should not be overlooked, however, is the importance of the first order character of the conventional spectrum in controlling the positions and intensities of the resonances due to strong coupling. We would thus like to communicate the results obtained from our analysis of the ^1H -2DJ nmr spectrum of 1,6-diazathianthrene (1) and the predicted influence of spectrometer operating frequency on the positions and intensities of the resonances due to strong coupling.



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Work by Freeman and co-workers has described the origins of resonances due to strong coupling in homonuclear 2DJ nmr spectra (4). Briefly, resonances due to strong coupling arise in 2DJ spectra as a direct consequence of

the application of the non-selective 180° pulse applied midway through the evolution period of the 2DJ see experimental (7). Thus, coherent magnetization associated with a given transition, for example, ν_{pq} is converted into a family of magnetization components of the type: ν_{rs} , ν_{tu} , ..., etc. which lead to responses at frequencies $\frac{1}{2}(\nu_{rs} - \nu_{pq})$, $\frac{1}{2}(\nu_{tu} - \nu_{pq})$, ..., etc. As a direct result of strong coupling, 2DJ spectra obtained for molecules with strongly coupled spin systems are frequently more complex than would be anticipated if the mixing of the basis functions by the non-selective 180° is not considered.

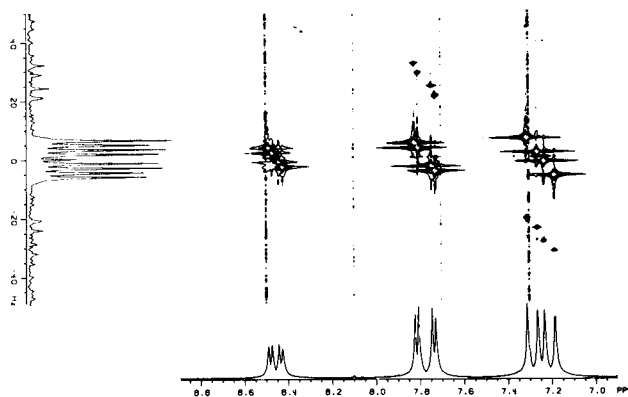


Figure 1. Contour plot of the $S(F_2, F_1)$ data matrix from the 2DJ-resolved ^1H -nmr spectrum of 1,6-diazathianthrene (1). The 0° projection (horizontal centered on 0 Hz) shows the "J-spectrum", the 90° projection (vertical) shows the normal spectrum.

The ^1H -2DJ nmr spectrum of 1,6-diazathianthrene (**1**) (8) was obtained using an initial $S(t_1, t_2)$ data matrix comprised of 256×1024 data points (9) which was processed to yield a final $S(F_2, F_1)$ data matrix consisting of 512×256 data points. The $S(F_2, F_1)$ data matrix provided the data which served as the basis for the analysis which follows.

A four level contour plot of the $S(F_2, F_1)$ data file for the ^1H -2DJ nmr spectrum of **1** is shown in Figure 1. In addition to the normal twelve line pattern for the A, B and X spins symmetrically disposed about $F_1 = 0$ Hz, eight additional responses were also observed in the AB region of the two-dimensional spectrum, these resonances arising due to strong coupling. Utilizing the conventional expressions for the analysis of an ABX spin system (10) (Equations 1-4)

$$2D_+ \cos 2\theta_+ = (\nu_A - \nu_B) + \frac{1}{2}(J_{AX} - J_{BX}) \quad \text{Eqn. 1}$$

$$2D_+ \sin 2\theta_+ = J_{AB} \quad \text{Eqn. 2}$$

$$2D_- \cos 2\theta_- = (\nu_A - \nu_B) - \frac{1}{2}(J_{AX} - J_{BX}) \quad \text{Eqn. 3}$$

$$2D_- \sin 2\theta_- = J_{AB} \quad \text{Eqn. 4}$$

expressions which allow the computation of the values of D_+ and D_- may be obtained (Equations 5 and 6)

$$2D_+ = \{[(\nu_A - \nu_B) + \frac{1}{2}(J_{AX} - J_{BX})]^2 + J_{AB}^2\}^{1/2} \quad \text{Eqn. 5}$$

$$2D_- = \{[(\nu_A - \nu_B) - \frac{1}{2}(J_{AX} - J_{BX})]^2 + J_{AB}^2\}^{1/2} \quad \text{Eqn. 6}$$

Using these fundamental expressions, all of the quantities necessary for computation of the frequencies and intensities in the 2DJ spectrum are accessible. Using the

Table I

Calculated and Observed Frequencies and Intensities for the ABX Spin System of 1,6-Diazathianthrene (**1**) in Deuteriochloroform at 100 MHz.

Resonances in the AB Region of the Spectrum						
Trans. Line	Calcd. F_A	Calcd. F_2 (a)	Obs. F_1	Obs. F_2	Calcd. I	Obs. I
1368	-6.31	718.49	-6.25	718.74	0.982	0.831
2547	-1.58	723.22	-1.55	723.57	0.974	0.913
1458	-4.76	773.35	-4.70	773.22	0.974	0.814
2637	-3.13	774.98	-3.10	774.34	0.982	0.938
1358	21.12	773.35	20.96	773.22	0.147	0.129
2537	24.30	774.98	24.22	774.34	0.147	0.163
2647	-29.01	723.22	-28.79	723.57	-0.126	-0.125 (b)
1468	-32.19	718.49	-32.07	718.74	-0.126	-0.088 (b)
6813	6.31	731.12	6.26	731.43	0.982	1.000
4725	1.58	726.39	1.56	726.67	0.974	0.910
5814	4.76	782.88	4.72	782.67	0.974	0.853
3726	3.13	781.25	3.12	781.06	0.982	0.960
5813	-21.12	731.12	-20.86	731.43	0.147	0.114
3725	-24.30	726.39	-24.22	726.67	0.147	0.140
4726	29.01	781.25	28.79	781.06	-0.126	-0.116 (b)
6814	32.19	782.88	32.01	782.67	-0.126	-0.132 (b)
Resonances in the X Region of the Spectrum (c)						
7812	3.18	849.47	3.12	849.47	1.000	0.439
4635	-1.55	844.74	-1.55	844.75	0.978	0.467
1278	-3.18	843.11	-3.10	843.09	1.000	0.416
3546	1.55	847.84	1.56	847.84	0.978	0.459
3535	0.00	844.74			0.022	(d)
4646	0.00	847.84			0.022	(d)

$$J_{AB} = 7.89 \text{ Hz}; J_{AX} = 1.62 \text{ Hz}; J_{BX} = 4.74 \text{ Hz}$$

$$\nu_X = 846.29; \nu_A = 777.82; \nu_B = 725.10; \nu_A + \nu_B/2 = 751.46; \Delta\nu = 52.72$$

$$D_+ = 25.88; D_- = 27.43; \theta_+ = 4.39^\circ; \theta_- = 0.25^\circ$$

(a) Calculated relative to $\nu_A + \nu_B/2$. (b) Negative intensities were verified by the examination of phase sensitive slices of the 2DJ spectrum. (c) In addition to those responses shown, twelve additional responses are predicted in theory but have zero intensities in the present case. (d) Could not be observed at the signal to noise available because of tailing of the main resonances in the X region of the spectrum.

treatment of Kumar (3) or that of Freeman and co-workers (4) the responses were computed and are compared with those obtained experimentally in Table I. Results obtained in this fashion show a very favorable comparison between the predicted and experimental frequencies and intensities as did the data in the initial reports (3,4). More importantly, however, the computed data in Table I also leads to an appreciation of the importance of first order character in the conventional spectrum controlling the displacement of resonances due to strong coupling relative to $F_1 = 0$ Hz and their intensities. In particular, this understanding evolves from a comprehension of the importance of the term $\nu_A - \nu_B$ in controlling the values of D_+ and D_- in Equations 5 and 6 and the values of the angles θ_+ and θ_- in Equations 7 and 8 which follow (11):

$\tan 2\theta_+ = J_{AB}/\Delta\nu + \frac{1}{2}(J_{AX} - J_{BX})$ Eqn. 7

$\tan 2\theta_- = J_{AB}/\Delta\nu - \frac{1}{2}(J_{AX} - J_{BX})$ Eqn. 8

where the term $\Delta\nu$ is defined by the expression

$$\Delta\nu = \nu_A - \nu_B \quad \text{Eqn. 9}$$

Thus, as the term $\Delta\nu$ in Hz in Equations 5-8 decreases, the terms D_+ and D_- decrease and the angles θ_+ and θ_- increase. The consequences of these trends in terms of the intensity and frequency of the responses may be summarized as follows: as the sum of the angles (θ) varies from

0° to a maximum of 90° , the intensity of the first order lines (the responses in the 2DJ spectrum corresponding to the normal one-dimensional responses) in the 2DJ spectrum shifts to those of higher order origin; as D_+ and D_- diminish in value, the frequencies of the higher order lines (those due to strong coupling) shift toward $F_1 = 0$ Hz. A numerical illustration of this trend is provided by Table II. As $\Delta\nu$ decreases from 52.72 Hz at 100 MHz to 31.63 Hz at 60 MHz, the D_\pm terms show a corresponding decrease accompanied by an increase in the angles θ_\pm .

The effects produced by this change are perhaps most tangibly seen by examining the consequent shift in the positions and intensities of the resonances due to strong coupling. Thus, the resonances due to strong coupling at 100 MHz which appear at 32.03, 28.79, 24.22 and 20.96 (calculated 32.19, 29.01, 24.30 and 21.12) Hz are shifted inward to calculated frequencies in F_1 of 21.84, 18.67, 13.94 and 10.76 Hz. The intensities of these resonances also exhibit a substantial change in intensities going from -0.132, -0.116, +0.163 and +0.129 (calculated -0.126, -0.126, +0.147 and +0.147) to calculated intensities of -0.184, -0.184, +0.238 and +0.238. In contrast, going from 100 MHz to higher observation frequencies produces a similar change but in the opposite sense: the positions of the strong coupling resonances shift outward from $F_1 = 0$ Hz accompanied by a diminution in intensity.

Table II

Computed Values for the Fundamental Parameters D_+ , D_- , θ_+ , θ_- , Σ and Δ as a Function of the Observation Frequency Accompanied by the Predicted Frequencies and Intensities of the Resonances Due to Strong Coupling at Each Spectrometer Frequency

	Spectrometer Frequency (MHz)					
	60	100	150	200	270	360
$\nu_A - \nu_B$	31.63	52.72	79.08	105.44	142.34	189.79
D_+	15.54	25.88	38.96	52.09	70.50	94.20
D_-	17.06	27.43	40.52	53.65	72.06	95.76
θ_+	7.35°	4.39°	2.91°	2.17°	1.60°	1.20°
θ_-	6.69°	4.14°	2.79°	2.11°	1.57°	1.18°
$\Sigma(\theta_+ + \theta_-)$	14.04°	8.53°	5.70°	4.28°	3.17°	2.38°
$\Delta(\theta_+ - \theta_-)$	0.66°	0.25°	0.12°	0.06°	0.03°	0.02°
1468 (a)	21.84/-0.184	32.19/-0.126	45.28/-0.089	58.41/-0.069	76.82/-0.053	100.52/-0.040
2647 (a)	18.67/-0.184	29.01/-0.126	42.09/-0.089	55.23/-0.069	73.64/-0.053	97.34/-0.040
2537 (a)	13.94/ 0.238	24.30/ 0.147	37.39/ 0.099	50.51/ 0.075	68.93/ 0.056	92.63/ 0.042
1358 (a)	10.76/ 0.238	21.12/ 0.147	34.21/ 0.099	47.34/ 0.075	65.75/ 0.056	89.45/ 0.042

(a) Frequency/intensity: frequencies in F_1 (Hz) also have mirror image counterparts.

Although the behavior predicted for resonances due to strong coupling remains to be experimentally verified by the examination of the same sample at two or more observation frequencies, the congruence between the calculated and observed frequency and intensity information in this and previous studies (3-6) would seem to strongly support this contention. Work is at present underway in this laboratory to experimentally verify this observation and will form the basis for a forthcoming report.

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(9) The sizes of the two-dimensional matrices are specified in numbers of data points in the order of the terms given. Thus, the $S(t_1, t_2)$ data matrix, which is specified as being 256×1024 data points consists of 256 points in t_1 by 1024 points in t_2 .

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