A Graphic Method for the Semi-quantitative Analysis of First-order Multiplet Spectra in Chemically Induced Dynamic Nuclear Polarization

By K. Müller

(*Department of Chemistry, The University of Chicago, Chicago, Illinois* 60637)

Summary The analysis of first-order CIDNP multiplet spectra can be easily carried out on a semi-quantitative level with the help of a graphic procedure which is summarized in a set of simple rules.

The qualitative analysis of CIDNP spectra[1-3] has been greatly facilitated by two simple sign rules derived independently by Trifunac[4] and Kaptein.[5] However a more detailed interpretation of CIDNP multiplet spectra still requires rather laborious numerical analyses or a computer simulation of the n.m.r. spectrum. We present here a graphic procedure providing a semi-quantitative analysis of first-order CIDNP multiplet spectra.

As an example we first consider an A_3X spin system

(Figure 1). The relative intensities of the four polarized X quartet lines are essentially determined by (i) the electronic Zeeman energy difference between the two radicals, $G = 0{\cdot}5\beta H_0\Delta g$ (note that $\Delta g = g_1 - g_2$ where g_1 is always associated with the radical carrying the X proton), (ii) the nuclear-electronic hyperfine coupling constants of the X proton a_X and the A_3 protons a_A, and (iii) the scalar electron-exchange coupling constant J.† A simultaneous plot of the four relative intensities I_{rel} *versus* G, where G is expressed in units of $0{\cdot}25\,|a_A|$, allows prediction of the shape of the polarized X quartet for any pair of a_A and Δg values‡ for a given set of a_X and J values. Such diagrams are readily obtained for any A_nX spin system with the help of the following simple rules:

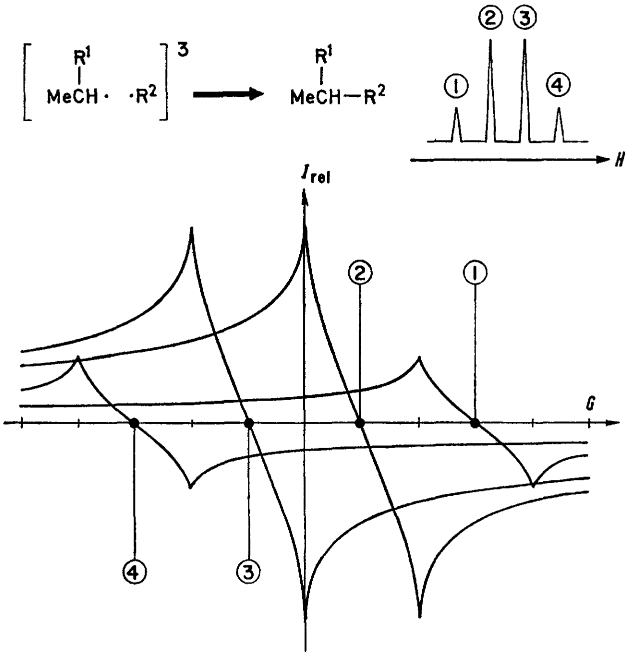

FIGURE 1. *Diagram representation for the relative line intensities of the* X *quartet of an* A_3X *spin system in a 'cage' recombination product schematically indicated above.* ($G = 0{\cdot}5\ \beta H_0\Delta g$, *in units of* $0{\cdot}25|a_A|$, *with* $|a_X| = |a_A|$ *and* $J = 0$.)

Rule 1: all the $(n + 1)$ I_{rel} (G) curves have identical characteristics;

Rule 2: they are symmetrically displaced along the G axis with a constant interval of two diagram units ($G = 0$ being a centre of symmetry);

Rule 3: their amplitudes are weighted by the binomial coefficients characterizing the relative line intensities of the corresponding X multiplet at thermo-equilibrium;

Rule 4: their shape is obtained from the following procedure (based on CIDNP formulae in refs. 2 and 6) given for one I_{rel} (G) curve where the case with $|a_X| = |a_A|$ and $J = 0$ is considered first (Figure 2, $p = 1$).

The I_{rel} (G) curve is centrosymmetric with respect to its zero point having a sharp maximum and minimum one diagram unit to the left and right of the zero point respectively and forming nearly horizontal wings further out. To a high degree of accuracy the shape of the curve may be obtained by connecting the extrema by a straight line and by approximating the initial curvature of the wings using the additional points one and two further units away where the amplitude reduces to *ca.* 50 and *ca.* 40% of its corresponding extreme values, respectively.

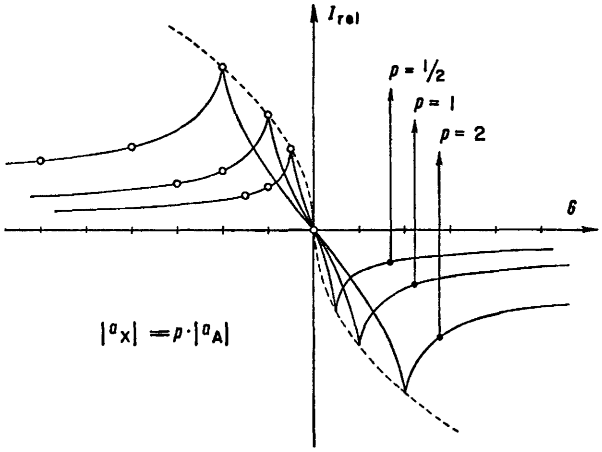

FIGURE 2: $I_{rel}(G)$ *curve as a function of the ratio* p ($J = 0$).

The change of the curve due to a variation of a_X is described in terms of the ratio $p = |a_X| / |a_A|$. Figure 2 shows that (i) any variation of $|a_X|$ does not shift the position of the zero point and (ii) all the characteristic features of the curve remain unchanged except that the total curve is contracted or expanded by the proportionality factor p.§

The effects of a non-vanishing electron-exchange coupling constant J can be summarized as follows: first, the position of the zero point is not affected. Further, the shape of the curve remains practically unchanged as long as $|J| < 0{\cdot}1\,|a_A|$. Higher values of $|J|$ result in a distinct broadening of the curve, a change which is most pronounced if $|J|$ and $|a_A|$ are comparable in magnitude, whereas for $|J| > |a_A|$ I_{rel} (G) soon approaches a straight line over an extensive region of the diagram. Numerical analysis shows that for $0{\cdot}5 < p < 2$ the (considerably rounded) extrema are shifted by about one diagram unit outwards from their original position if $|J| = 0{\cdot}5\,|a_A|$ and by about two diagram units if $|J| = |a_A|$.¶

The general shape of the $I_{rel}(G)$ curves is thus determined except for their 'phase' which is defined by the sign of the slope at their zero points. The 'phase' is given by rule 5** where (a_X) is the absolute sign of a_X, (μ) is the sign

---

† This parameter has been assumed essentially to vanish;[6] however it has also been used as an adjusting parameter[2] to give best fits between experimental and computer-simulated spectra.

‡ Note that for CIDNP multiplets obtained at 60 MHz one diagram unit corresponds to $\Delta g = 7{\cdot}10^{-5}|a_A|$ if a_A is given in gauss.

§ The fact that the amplitude of I_{rel} (G) increases with $\sqrt{p}$ is of minor importance since we are only concerned about relative line intensities within a multiplet.

¶ For $p < 0{\cdot}5$ I_{rel} (G) is more sensitive whereas for $p > 2$ it is less sensitive towards a variation in $|J|$.

** Rules 5 and 6 contain the same sign parameters previously used[3-5] for the qualitative CIDNP rules. Note however that by definition sign(l) = − sign(σ), σ being the location parameter used by Kaptein.[5]

of the multiplicity parameter (+ for triplet precursor, − for singlet precursor), and (c) indicates the sign of the 'cage' parameter (+ for 'cage' products, − for products from radicals that escaped the 'cage'). Thus the 'phase' of the curves in Figure 1 is negative if $a_X < 0$.

Rule 5: $(a_X)\cdot(\mu)\cdot(c)$ = 'phase' of the I_{rel} (G) curves;

Rule 6: $(a_A)\cdot(J_{AX})\cdot(l)$ = sign of the labelling sequence.

To complete the diagram we have to specify the labelling sequence of the $(n + 1)$ curves which is defined as positive if the numbers increase in the same and negative if in the opposite direction compared to the labels of the multiplet lines in the spectrum. The sign of the labelling sequence is given by rule 6** where (a_A) and (J_{AX}) are the absolute signs of a_A and the nuclear coupling constant J_{AX} respectively, and (l) indicates the sign of the location parameter (+ if protons A_n and X were located on different radicals, − if they were on the same radical). Thus the labelling sequence in Figure 1 is negative for $a_A > 0$ and $J_{AX} > 0$.

Finally, in the general case of an A_nX_m spin system the diagram for the polarized X multiplet is obtained by analogy with the corresponding A_nX spin system, the only difference being that each curve is now a composite of N components. The characteristics of each component are identical and again determined by the procedure of rule 4 except that the components are expanded by the proportionality factors $f = m, m - 2, m - 4, \cdots$ where the condition $f > 0$ determines the number N. They are weighted in the ratio $b_1f_1 : b_2f_2 : \cdots : b_Nf_N$ where $b_1, b_2, \cdots, b_N$ are the first N binomial coefficients in $(1 + x)^m$ and $f_1, f_2, \cdots, f_N$ are the corresponding expansion factors. Accordingly, the diagram for the X multiplet of an A_nX_2 spin system differs from that of the corresponding A_nX spin system *only* in that all the curves are expanded by a factor of $f = 2$, whereas in the case of an A_nX_3 spin system each curve is the sum of two equally weighted components with expansion factors $f = 3$ and $f = 1$.

In this generalized form the diagram procedure provides an easy analysis of both the X and the A multiplet of any A_nX_m spin system and renders a quick estimate of the spectral changes due to parameter variations (and hence structural modifications). It also facilitates the discussion of further factors which may influence relative line intensities (such as the presence of additional paramagnetic nuclei in the radicals or nuclear spin relaxation in the diamagnetic product[7]) and should therefore prove valuable not only in analysing but also in designing new CIDNP experiments.

I thank Professor G. L. Closs for stimulating discussions and the Stiftung für Stipendien auf dem Gebiete der Chemie and the Petroleum Research Fund for financial support.

(*Received, August* 19*th,* 1971; *Com.* 1464.)

---

[1] J. Bargon, H. Fischer, and U. Johnson, *Z. Naturforsch.*, 1967, **22a**, 1551; H. R. Ward and G. R. Lawler, *J. Amer. Chem. Soc.*, 1967, **89**, 5518; G. L. Closs, *ibid.*, 1969, **91**, 4552; R. Kaptein and L. J. Oosterhoff, *Chem. Phys. Letters*, 1969, **4**, 195, 214.

[2] R. Kaptein, "Chemically Induced Dynamic Nuclear Polarization", Ph.D. thesis, Leiden University, 1971.

[3] G. L. Closs, *Pure Appl. Chem.*, in the press.

[4] A. D. Trifunac, Ph.D. thesis, Chicago University, 1971, p. 109.

[5] R. Kaptein, *Chem. Comm.*, 1971, 732.

[6] F. J. Adrian, *J. Chem. Phys.*, 1970, **53**, 3374; *ibid.*, 1971, **54**, 3912.

[7] G. L. Closs and K. Müller, to be published.