Two-dimensional Two Contact Double Resonance Spectroscopy

David Stephenson

Chemistry Dept., Faculty of Agriculture and Natural Sciences, University of the West Indies,
St. Augustine, Trinidad and Tobago

Reprint requests to Dr. D. St.; Fax: 868 663 9686; E-mail: david@chem.uwi.tt

Z. Naturforsch. **55 a,** 79–82 (2000); received September 11, 1999

*Presented at the XVth International Symposium on Nuclear Quadrupole Interactions,
Leipzig, Germany, July 25 - 30, 1999.*

A two-dimensional spectroscopic technique is presented. Application of the technique to determine all the relaxation rates for a multi-level quadrupole system is discussed along with experimental requirements. Theoretical and experimental data are analyzed for the ^{14}N, three level, spin 1 system. The analysis shows that all three relaxation rates can be obtained from a single two-dimensional spectrum, and that only 3 peaks in the 3×3 two-dimensional intensity matrix are needed to completely specify the problem. The 4-level spin 3/2 system is also examined. In theory, all six relaxation rates can be independently evaluated (for a suitable system) without necessitating measurement at the low frequency Zeeman separated levels.

Key words: NQR; ^{14}N; Relaxation; Two-dimensional; Cross-relaxation.

Introduction

Nuclear quadrupole energy level systems present an interesting challenge from the point of view of relaxation studies. For even in simplest case of a three level system the relaxation is biexponential. For an N-level system the decay should be $(N-1)$-exponential, each of the exponents being a mixture of the $N(N-1)/2$ independent relaxation rates. The difficulty of separating exponentials is well known and is particularly difficult when the two exponents are of similar magnitude. Indeed, often a convincing fit to a single exponential can be obtained for these multilevel systems, the individual relaxation rates being hidden within the single value exponent. Even in the case where the components of a biexponential can be extracted there is insufficient information in these exponents to allow determination of the individual relaxation rates. If relaxation rates between each pair of levels could be determined a much clearer picture of the processes responsible for the relaxation could be obtained. This paper presents a theoretical analysis of a two-dimensional variation of the previously described technique of double contact cross-relaxation [1, 2]. The technique in theory allows the $N(N-1)/2$ relaxation rates for an N-level system to be determined. Experimentally this ideal cannot always be realized because of Zeeman broadening which is a characteristic of cross-relaxation detection. For integral spin nuclei the Zeeman effect is not a problem (except for zero η) but for half-integer spin nuclei it is desirable to work with nuclei that have small magnetogyric ratios and low quadrupole resonance frequencies. The application of the technique to obtain the three relaxation rates for the three level ^{14}N system will be demonstrated, and the extension of the technique to more complex systems will be discussed.

Experimental

All calculations were carried out on an ordinary PC (Digital DEC 466). Because the matrices are small, Jacobi's method was used for the diagonalization. This method is computationally easy to implement and shows high stability. The average (absolute) intensity of off-diagonal peaks (starting from the normalized intensity matrix) was reduced to 2×10^{-5}. Single precision arithmetic was used throughout.

Discussion

It is convenient to divide the double contact cross-relaxation experiment into three phases: polarization, evolution and detection. Polarization takes place immediately after the sample leaves high field, the proton energy levels and a pair of quadrupole levels are brought into contact by an appropriately chosen cross-relaxation field; Rapid energy exchange takes place polarizing the Q spins. In the second phase (evolution) the stored magnetization is allowed to evolve according to the individual relaxation rates within the quadrupole energy level system. Detection takes place when a cross-relaxation field is reapplied. Transfer of the sample back to high field completes the double resonance cycle. To record a normal spectrum, both contacts will be at the same magnetic field (and hence frequency) and the time spent in zero field will be kept to a minimum to prevent relaxation losses. However if both cross-relaxation fields can be swept independently, a two-dimensional spectrum can be built up with one axis being the polarization frequency and the other being the detection frequency. Furthermore, if the sample is left for an appropriate period in zero field, the peak intensities will contain complete information on the relaxation rate between all levels of the quadrupole system. Only a few points in the two-dimensional spectrum will have a non-zero signal, so the experiment can concentrate on these and need not be too time consuming.

Three-level System

The simplest case to study is a three level system, for example ^{14}N. Zeeman broadening at the cross-relaxation condition (except for zero η cases) can be ignored for this nucleus. For such a system 9 non-zero points can be observed in the 2D spectrum forming a 3×3 intensity matrix. As the matrix is symmetric, only the upper triangle need be recorded. There is further redundancy in the matrix because the intensity of the ν_0 peak plus the intensity of the ν_- line equals the ν_+ intensity. So, knowing two values in any row or column, the third value can be obtained algebraically. This means that only three values need be recorded to construct the full 3×3 intensity matrix. Analysis of the intensity matrix can be carried out in a similar manner to a two-dimensional NMR exchange spectrum [3, 4]. But there are two major differences; first the initial intensity matrix is not diagonal, and second we are measuring population differences. These differences cause each element of the relaxation matrix to be a linear combination of all three relaxation rates. Furthermore in order to determine correct eigenvalues the intensity matrix has to be normalized. At time zero, adding the absolute intensities (ignoring negative signs) of peaks in the upper triangle of the matrix should give an answer of 3, the same as the number of rows (or columns) in the matrix. Matrices recorded with different delay times are scaled according to this, and absolute relaxation rates can be calculated. Only relative rates can be obtained if this normalization step is not included. Measurement of the total matrix intensity at time zero can be achieved by measuring the intensity of the ν_+ peak with no (or minimal) evolution time. At time zero all the peak intensities are algebraically related. It is also a good idea to measure the ν_- and ν_0 peaks to ensure that there is equal cross-relaxation efficiency for all levels. If this is not the case appropriate scaling of rows and columns in the two-dimensional spectrum will be needed.

The differential equations describing a three level system can be readily solved (an elegant solution can be found in [5]). Using this solution it can be shown that the intensity of any peak in the 2D spectrum can be expressed:

$$I_{ij} = A_{ij} e^{k\tau} + B_{ij} e^{m\tau}$$

τ (the evolution time) is the time elapsed between the two cross-relaxation contacts. So all the peaks decay according to the same two exponents. The exponents are the eigenvalues of the intensity matrix, and the multiplying constants (A and B) are related to the eigenvectors.

The matrix of relaxation rates can be expressed by a similar equation:

$$R_{ij} = A_{ij} k + B_{ij} m.$$

Using matrix algebra the problem can be readily solved:

$$I = X \cdot \Lambda \cdot X^{-1}, \quad R = X \cdot \ln(\Lambda)/\tau \cdot X^{-1},$$

where Λ is a diagonal matrix formed from the diagonalization of the 2D spectrum intensities (I), X is the eigenvector matrix and X^{-1} its inverse (in this case $X^{-1} = X^{\mathrm{T}}$). There are only two non-zero elements in the Λ array as the problem has only two eigenvalues.

The 3×3 matrix R contains relaxation transition probabilities. Each element is a combination of all the relaxation rates. The exact form is determined by the starting conditions. If J is the normalized intensity matrix at time zero and W_1, W_2 and W_3 are the three relaxation rates corresponding to the ν_+, ν_- and ν_0 transitions, respectively, then

$$-\frac{R_{ij}}{3} = W_1 \times J_{i1} \times J_{j1} + W_2 \times J_{i2} \times J_{j2} + W_3 \times J_{i3} \times J_{j3}.$$

The problem can be solved algebraically, but it is better to treat the R matrix as an overdetermined set of linear equations and find the least squares solution (a good description of the method can be found in [6]). It is interesting to note that reversing the non-zero eigenvalues gives a much simpler R matrix. Each off-diagonal element depending on only one relaxation rate. The least squares method is, however, prefered as it includes all matrix elements in the determination of the relaxation rates.

Predetermination is avoided by not using the same equations to generate data as were used in the solution. Instead, theoretical two-dimensional intensity data were generated numerically from the rate equations using 100 equal time intervals from zero to the evolution time. The following are the intensity matrices at τ = 0 and τ = 0.1 s using relaxation rates W_1 = 1 s^{-1}, W_2 = 2 s^{-1} and W_3 = 3 s^{-1}. Both matrices have been multiplied by 3. (The mathematical rather than the spectroscopic convention has been used, so the diagonal runs from top left to bottom right).

$$I \times 3(\tau = 0\text{s}) = \begin{array}{cccc} & \nu_+ & \nu_- & \nu_0 \\ \nu_+ & 2 & 1 & 1 \\ \nu_- & 1 & 2 & -1 \\ \nu_0 & 1 & -1 & 2 \end{array},$$

$$I \times 3(\tau = 0.1\text{s}) = \begin{array}{cccc} & \nu_+ & \nu_- & \nu_0 \\ \nu_+ & 1.28 & 0.72 & 0.56 \\ \nu_- & 0.72 & 1.11 & -0.38 \\ \nu_0 & 0.56 & -0.38 & 0.95 \end{array}.$$

Diagonalization gives Λ = 0.652, 7.0×10^{-8} and 0.460. ln(Λ)/τ = –4.28, zero and –7.76 (the smallest value is always zeroed).

The calculated R matrix is:

$$R = \begin{array}{ccc} -3 & -1 & -2 \\ -1 & -4 & 3 \\ -2 & 3 & -5 \end{array}.$$

A least squares analysis returns the original values for the relaxation rates. Random variation of the input intensities by up to ±10% propagates into an error in the calculated W's of about ±10%. It should be noted, however, that the evolution time has been optimized and there is not a large dynamic range in the relaxation rates used. If the relaxation rates are very different then measurement at two evolution times may be necessary to obtain acceptable answers. When the signal to noise ratio reaches about 1:1, eigenvalues can become negative, which renders the data impossible to analyze.

A three level system can be analyzed from the diagonal peaks alone. The number of off-diagonal elements in the upper triangle does not exceed the number of diagonal elements. One-dimensional spectra have been previously presented for 4-nitrobenzoic acid [1]. A relaxation analysis was carried out on the basis of decays rates (using 20 delay times). It was assumed that two of the three relaxation rates were equal and the third small [1, 7]. Using the two-dimensional approach it is possible to determine the three relaxation rates without such provisos and with only one (suitably chosen) delay time. The diagonal peaks ν_+, ν_- and ν_0 at time zero had intensities of 200, 167, and 124. From which it can be deduced that cross-relaxation was not as effective at ν_0 and ν_- peaks as at ν_+. If it is assumed that a constant proportion of the magnetization is measured, for each peak the peak intensities can be corrected. The peak heights are adjusted to give 200, 200, and 200 at time zero. The off-diagonal peaks are obtained using the relations

$$I_{12} = I_{21} = \frac{1}{2}(I_{11} + I_{22} - I_{33}),$$

$$I_{13} = I_{31} = \frac{1}{2}(I_{11} - I_{22} + I_{33}),$$

$$I_{23} = I_{32} = \frac{1}{2}(I_{11} - I_{22} - I_{33}).$$

Analysis of the matrix formed gives the results shown in Table 1. For both evolution times the calculated relaxation rates are the same within experimental error. The results are consistent with the previous analysis [1]. Using this method it is possible to show that relaxation between the levels 0 and +1 (ν_+) is slightly slower than for relaxation between the 0 and –1 levels (ν_-). (The previous analysis [1] had to assume these rates were equal). Furthermore the relaxation rate between the +1 and –1 levels (ν_0) is determined as being (almost) zero. The much larger relaxation rate quoted in [1] can again be traced to the assumptions made in that analysis.

Table 1. Intensities of the diagonal peaks in the two-dimensional cross-relaxation spectrum of 4-nitrobenzoic acid and the results of a relaxation analysis (see text). For comparison: In [1] relaxation rates of 0.035, 0.035 and 0.007 s^{-1} are given. (Note: relaxation time T_1 = 1/2W).

Evolution time (s)	Transition	Diagonal Intensity	Relaxation (s^{-1})	Relaxation time (s)
5	ν_+	124.6	0.0378	13.2
5	ν_-	119.5	0.0429	11.7
5	ν_0	160.7	0.0017	294
8	ν_+	92.5	0.0379	13.2
8	ν_-	87.9	0.0437	11.4
8	ν_0	140.7	0.0016	312

Four-level System

As an example a spin, 3/2 nucleus in a nonzero magnetic field will be considered. An example that possesses the desirable characteristics of a low resonance frequency and a small magnetogyric ratio is ^{39}K. A Zeeman field (away from the cross-relaxation condition) should be maintained during the evolution time to prevent the system from degenerating to a 2-level system. It may be possible to investigate the variation of the relaxation rates with the applied magnetic field. The intensity matrix is 6×6 but once again there is some redundancy. Only 3 elements in each row and column need be collected. So the relative populations of the 1/2 –1/2 pair and the 3/2 –3/2 pair of levels can be obtained from measurements of the other transitions. This is quite fortunate as these pairs of levels never satisfy the cross-relaxation condition. The analysis can be carried out in exactly the same way as for a three level system. The normalization condition once again requires that at time zero the total (absolute) intensity of the upper triangle be equal to the number of rows in the matrix, namely 6. Test data were generated numerically (as described above). As expected three of the six eigenvalues are zero – the relaxation is triexponential. The three lowest values in the diagonal Λ matrix should be zeroed. The final R matrix can be analyzed in the same way as for a three level system. Each element in the matrix is a linear combination of six relaxation rates, so analyzing the matrix directly using the least squares method is almost inescapable.

There is an extra complication for studies of half-integral spin nuclei in polycrystalline samples. The cross-relaxation frequency will be determined by the orientation the crystal axes make with the magnetic field. This may be turned to advantage as the orientational dependence of the relaxation rates could be investigated.

For half-integral spin nuclei with large magnetogyric ratios it should be possible to obtain some relief from the effects of a weakened cross-relaxation signal. By modulating the cross-relaxation field a range of crystal orientations could be made to exchange polarization with the protons, thereby increasing the storage capacity of the Q system.

[1] D. Stephenson and J. A. S. Smith, J. Chem. Soc., Faraday Trans. 2, **83**, 2123 (1987).
[2] D. Stephenson and J. A. S. Smith, Z. Naturforsch. **55a**, 37 (2000).
[3] C. L. Perrin and R. K. Gipe, J. Amer. Chem. Soc. **106**, 4036 (1984).
[4] E. W. Abel, T. J. P. Coston, K.G. Orrell, V. Sik, and D. Stephenson, J. Magn. Reson. **70**, 34 (1986).
[5] A. R. Forsyth, A Treatise on Differential Equations, 6th Ed. Macmillan, London 1929, pp. 438.
[6] G. Dahlquist and Å. Björck, Numerical Methods, Chapt. 5.7, Prentice-Hall, Englewood Cliffs, N. J. 1974.
[7] D. Stephenson, PhD. Thesis, University of London (1986).