

# Nuclear spin-waves, multiple quantum NMR, and the benzene ring

G.J. Bowden

*Department of Physics and Astronomy, University of Southampton, Highfield,  
Southampton SO17 1BJ, UK*

Received 9 July 2002

In the description of multiple quantum NMR spectra of spin  $\frac{1}{2}$  coupled nuclear spin systems, the interpretation is greatly simplified by subdividing the Hamiltonian  $\mathcal{H}$  ( $= \mathcal{H}_1 + \mathcal{H}_2$ ), where  $\mathcal{H}_1$  is a suitable combination of the constants of the motion. In this paper, a useful connection is established between (i) the discrete Fourier transform, (ii) the Bloch theorem for translationally invariant systems, and (iii) the nuclear spin dynamics of the benzene ring. In particular, it is shown that multiple quantum NMR experiments, performed at room temperature, can be used to probe the nuclear spin-wave excitations ( $\sim 10^{-7}$  K) of the benzene ring.

## 1. Introduction

In three preceding papers [1–3], it was argued that the interpretation of multiple quantum NMR spectra of coupled spin  $1/2$  systems can be greatly simplified by dividing the Hamiltonian up into two parts:

$$\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2, \quad (1)$$

where (i)  $\mathcal{H}_1$  is chosen to be a suitable combination of the constants of the motion and (ii)  $\mathcal{H}_2 = \mathcal{H} - \mathcal{H}_1$ . In particular, it was shown that analytical solutions can be found for the eigenvalues and eigenvectors of the  $64 \times 64$  Hamiltonian matrix for six hydrogen nuclei of the benzene ring, thereby allowing a concise and in-depth description of multiple quantum NMR (MQ-NMR) experiments on oriented benzene [4–7]. It should also be noted that a complete solution for the benzene ring has also been given by [8], though in a completely different format, and approach, from this work and that of [1–3].

In this paper, the results of [3] are re-examined in the light of a connection between the Discrete Fourier Transform (DFT) and the unitary transformation used to diagonalise the  $6 \times 6$ ,  $15 \times 15$ ,  $20 \times 20$ ,  $\mathcal{J}_z = \pm 2, \pm 1$ , and  $0$  matrices of the benzene ring. It is shown that the eigenvectors can be interpreted in terms of collective Bloch wave excitations, such as those encountered in (i) the band theory of solids, (ii) the tight-binding approximation for transition metals, and (iii) spin-waves [9,10].

Finally, to avoid duplication, the definitions and terminology used below are identical to those of [3], which should be read in connection with this paper.

## 2. Unitary transformations and the Discrete Fourier Transform

In [3], it was shown that while the eigenvalues and eigenvectors of  $\mathcal{H}_1$  were trivial, those of  $\mathcal{H}_2$  require more effort. Nevertheless, in the secular approximation  $\mathcal{J}_z$  is a good quantum number, which allows the  $64 \times 64$  matrix in question to be block-diagonalised into the  $\mathcal{J}_z = \pm 2, \pm 1, 0, 6 \times 6, 15 \times 15, 20 \times 20$  matrices, respectively. For example, the  $6 \times 6$  matrix associated with  $\mathcal{J}_z = +2$  takes the form:

$$\mathcal{H}_2(\mathcal{J}_z = +2) = -\frac{1}{4} \begin{bmatrix} |A\rangle & |B\rangle & |C\rangle & |D\rangle & |E\rangle & |F\rangle \\ 0 & \alpha & \beta & \gamma & \beta & \alpha \\ \alpha & 0 & \alpha & \beta & \gamma & \beta \\ \beta & \alpha & 0 & \alpha & \beta & \gamma \\ \gamma & \beta & \alpha & 0 & \alpha & \beta \\ \beta & \gamma & \beta & \alpha & 0 & \alpha \\ \alpha & \beta & \gamma & \beta & \alpha & 0 \end{bmatrix}, \quad (2)$$

where (i)  $|A\rangle$  is a shorthand notation for all spins up except at position  $A$  on the benzene ring etc., and (ii)  $\alpha, \beta,$  and  $\gamma$  are dipolar interaction parameters, associated with nearest, next-nearest, and next-next-nearest interactions, respectively.

In [3], it was recognised that the matrix of equation (2) is a circulant, which can be diagonalised using a unitary transformation which reflects the six-fold symmetry of the benzene ring. A transformation, based on the character tables for the  $C_6$  group was therefore devised [11]. However, in this paper it is shown that there is a close connection between the transformation used by [3], and the Discrete Fourier Transform [12], widely used in the Cooley–Tukey algorithm [13]. In this paper, the latter is exploited to give maximal insight into the nuclear spin dynamics of the benzene ring.

The unitary matrix for a six-number DFT is given by:

$$\mathcal{U}_6 = \frac{1}{\sqrt{6}} \begin{bmatrix} 1 & 1 & 1 & 1 & 1 & 1 \\ 1 & \omega & \omega^2 & \omega^3 & \omega^4 & \omega^5 \\ 1 & \omega^2 & \omega^4 & \omega^6 & \omega^8 & \omega^{10} \\ 1 & \omega^3 & \omega^6 & \omega^9 & \omega^{12} & \omega^{15} \\ 1 & \omega^4 & \omega^8 & \omega^{12} & \omega^{16} & \omega^{20} \\ 1 & \omega^5 & \omega^{10} & \omega^{15} & \omega^{20} & \omega^{25} \end{bmatrix} = \frac{1}{\sqrt{6}} \begin{bmatrix} 1 & 1 & 1 & 1 & 1 & 1 \\ 1 & \omega & \omega^2 & -1 & \omega^4 & \omega^5 \\ 1 & \omega^2 & \omega^4 & 1 & \omega^2 & \omega^4 \\ 1 & -1 & 1 & -1 & 1 & -1 \\ 1 & \omega^4 & \omega^2 & 1 & \omega^4 & \omega^2 \\ 1 & \omega^5 & \omega^4 & -1 & \omega^2 & \omega \end{bmatrix}, \quad (3)$$

where (i)

$$\omega = e^{i2\pi/6} \quad (4)$$

and (ii) several identities have been used to arrive at the right-hand side of (3). The right-hand matrix is almost identical to that given by [3], except for relabelling of all the rows save that of row 1. In passing, we note that the DFT is usually applied in a Boolean framework where the dimension of the DFT is determined by  $\{2^n\}$ ,  $n$  integer. However, in the case of a molecule the size of the DFT is set by the number of spins in question.

If we apply the unitary transformation to the Hamiltonian of (2), we find:

$$\begin{aligned} \mathcal{H}_2(\mathcal{J}_z = +2)' \\ &= U_6 \mathcal{H}_2 U_6^{-1} \\ &= -\frac{1}{4} \begin{bmatrix} 2\alpha + 2\beta + \gamma & 0 & 0 & 0 & 0 & 0 \\ 0 & \alpha - \beta - \gamma & 0 & 0 & 0 & 0 \\ 0 & 0 & -\alpha - \beta + \gamma & 0 & 0 & 0 \\ 0 & 0 & 0 & -2\alpha + 2\beta - \gamma & 0 & 0 \\ 0 & 0 & 0 & 0 & -\alpha - \beta + \gamma & 0 \\ 0 & 0 & 0 & 0 & 0 & \alpha - \beta - \gamma \end{bmatrix} \end{aligned} \quad (5)$$

identical to that of equation (16) of [3], except for the order.

We are now in a position to discuss the significance of the wave-functions embodied in the unitary transformation of (3). If we apply the unitary transformation, to the wavefunctions used to generate the Hamiltonian (2), they take the general form:

$$|\psi\rangle = |A\rangle + \omega^r |B\rangle + \omega^{2r} |C\rangle + \omega^{3r} |D\rangle + \omega^{4r} |E\rangle + \omega^{5r} |F\rangle \quad (6)$$

for the six wavefunctions  $0 \leq r \leq 5$ . The analogy with the Bloch theorem for simple plane waves in metals can now be made by defining a wave-vector:

$$k_r = r \frac{2\pi}{6a}, \quad (7)$$

where  $a$  is the spacing between adjacent spins in the benzene ring. Consequently, equation (6) can be rewritten in the form:

$$|\psi\rangle = |A\rangle + e^{ik_r a} |B\rangle + e^{ik_r 2a} |C\rangle + e^{ik_r 3a} |D\rangle + e^{ik_r 4a} |E\rangle + e^{ik_r 5a} |F\rangle. \quad (8)$$

It is clear therefore that the transformed wavefunctions are simple spin-waves, characterised by a phase difference  $r(2\pi/6)$  between adjacent spins. Thus the nuclear excitations of the benzene ring, for the  $\mathcal{J}_z = +2$  state, can be described in terms of collective nuclear spin-wave states, with differing wavelengths  $\lambda_r = 2\pi/k_r$ . Further, the energy eigenvalues of equation (5) can be reinterpreted in terms of a collective dispersion relation  $E(k_r)$  vs.  $k_r$ . However unlike solids, the dispersion curve shown in figure 1, is now quite discrete. Note that in preparing this diagram, we have used both negative and positive wave-vectors  $k_r$ . This is possible because for  $k_1$  ( $k_2$ ) the spin-wave runs clockwise, with a phase separation  $\phi = \pi/3$  ( $\phi = 2\pi/3$ ) between adjacent spins, whereas for  $k_5$  ( $k_4$ ) the spin-wave runs anticlockwise with a phase separation of  $\phi = -\pi/3$  ( $\phi = -2\pi/3$ ), respectively. Thus  $k_5 = -k_1$  and  $k_4 = -k_3$ . Secondly, in preparing the

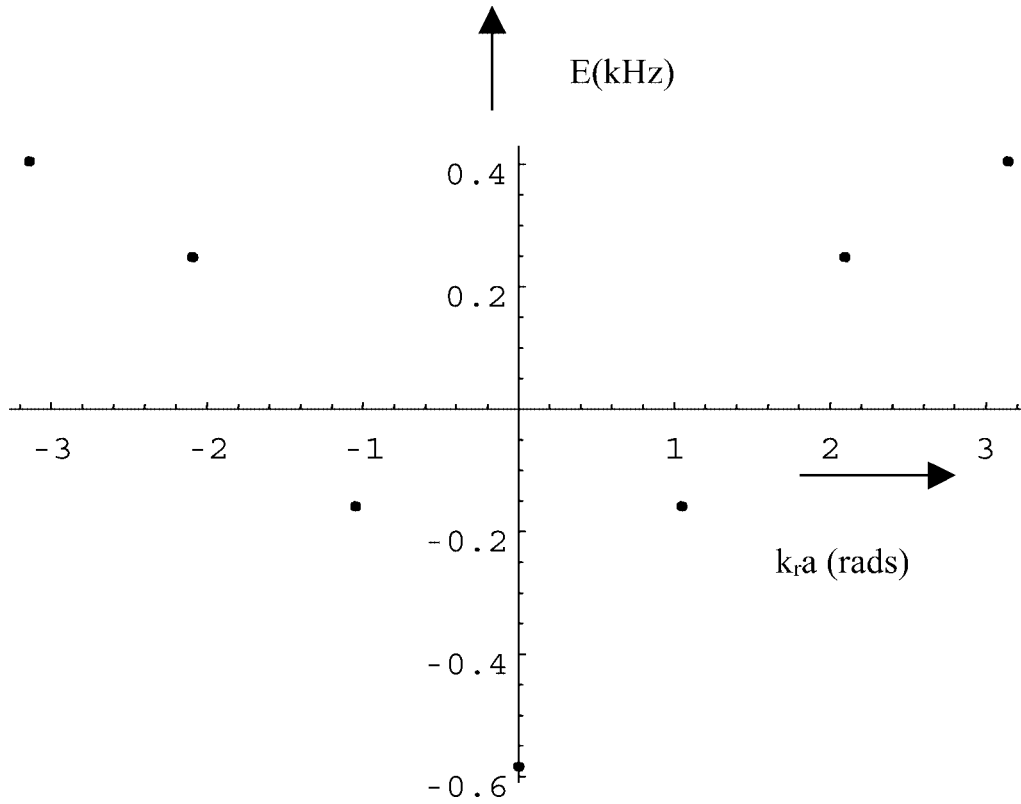


Figure 1. Nuclear spin-wave dispersion curve for the benzene ring.

energy scale shown in figure 1, we have used (i) the MQ-NMR interpretation of [3], who showed that:

$$\bar{D} = \frac{1}{5}[2\alpha + 2\beta + \gamma] = 0.431 \text{ (kHz)} \quad (9)$$

and (iii) the dipole-dipole relationships:

$$\beta = \frac{\alpha}{3\sqrt{3}} \quad \text{and} \quad \gamma = \frac{\alpha}{8} \quad (10)$$

for the benzene ring.

Note that (i) the lowest energy-state is given by  $k_0 a = 0$ , i.e., all the spins rotating in phase, and (ii) the zone boundaries occur at  $k_3 a = \pm\pi$ .

### 3. The two spin down case: $\mathcal{J}_z = +1$

The situation for the  $\mathcal{J}_z = +1$   $15 \times 15$  matrix, for the two-spin down case, is more complicated. In this instance it is interference between two spin-waves with the same wave vector which dominate events.

Following [3], the Hamiltonian for the  $\mathcal{J}_z = +1$  case is found to be:

$$\mathcal{H}_2(\mathcal{J}_z = +1) = -\frac{1}{4} \begin{pmatrix} \begin{bmatrix} \eta & \beta & 0 & 0 & 0 & \beta \\ \beta & \eta & \beta & 0 & 0 & 0 \\ 0 & \beta & \eta & \beta & 0 & 0 \\ 0 & 0 & \beta & \eta & \beta & 0 \\ 0 & 0 & 0 & \beta & \eta & \beta \\ \beta & 0 & 0 & 0 & \beta & \eta \end{bmatrix} & \begin{bmatrix} \alpha & \gamma & 0 & 0 & \gamma & \alpha \\ \alpha & \alpha & \gamma & 0 & 0 & \gamma \\ \gamma & \alpha & \alpha & \gamma & 0 & 0 \\ 0 & \gamma & \alpha & \alpha & \gamma & 0 \\ 0 & 0 & \gamma & \alpha & \alpha & \gamma \\ \gamma & 0 & 0 & \gamma & \alpha & \alpha \end{bmatrix} & \begin{bmatrix} \beta & \beta & 0 \\ 0 & \beta & \beta \\ \beta & 0 & \beta \\ \beta & \beta & 0 \\ 0 & \beta & \beta \\ \beta & 0 & \beta \end{bmatrix} \\ \begin{bmatrix} \alpha & \alpha & \gamma & 0 & 0 & \gamma \\ \gamma & \alpha & \alpha & \gamma & 0 & 0 \\ 0 & \gamma & \alpha & \alpha & \gamma & 0 \\ 0 & 0 & \gamma & \alpha & \alpha & \gamma \\ \gamma & 0 & 0 & \gamma & \alpha & \alpha \\ \alpha & \gamma & 0 & 0 & \gamma & \alpha \end{bmatrix} & \begin{bmatrix} \chi & 0 & \beta & 0 & \beta & 0 \\ 0 & \chi & 0 & \beta & 0 & \beta \\ \beta & 0 & \chi & 0 & \beta & 0 \\ 0 & \beta & 0 & \chi & 0 & \beta \\ \beta & 0 & \beta & 0 & \chi & 0 \\ 0 & \beta & 0 & \beta & 0 & \chi \end{bmatrix} & \begin{bmatrix} \alpha & 0 & \alpha \\ \alpha & \alpha & 0 \\ 0 & \alpha & \alpha \\ \alpha & 0 & \alpha \\ 0 & \alpha & \alpha \\ 0 & \alpha & \alpha \end{bmatrix} \\ \begin{bmatrix} \beta & 0 & \beta & \beta & 0 & \beta \\ \beta & \beta & 0 & \beta & \beta & 0 \\ 0 & \beta & \beta & 0 & \beta & \beta \end{bmatrix} & \begin{bmatrix} \alpha & \alpha & 0 & \alpha & \alpha & 0 \\ 0 & \alpha & \alpha & 0 & \alpha & \alpha \\ \alpha & 0 & \alpha & \alpha & 0 & \alpha \end{bmatrix} & \begin{bmatrix} \xi & 0 & 0 \\ 0 & \xi & 0 \\ 0 & 0 & \xi \end{bmatrix} \end{pmatrix}, \quad (11)$$

where the labelling, from left to right is  $|AB\rangle|BC\rangle|CD\rangle|DE\rangle|EF\rangle|FA\rangle$ ,  $|AC\rangle|BD\rangle|CE\rangle|DF\rangle|EA\rangle|FB\rangle$ , and  $|AD\rangle|BE\rangle|CF\rangle$ , respectively. The symbols used in equation (11) are defined in [3].

From an examination of equation (11) it is evident that the  $15 \times 15$  matrix is not a circulant. However, in partitioned form, the individual matrices are circulants, for both the square and nonsquare matrices.

As shown by [3], the Hamiltonian matrix of (11) can be brought to near diagonal form using the block diagonal  $15 \times 15$  unitary matrix:

$$\mathcal{U}_{15} = \mathcal{U}_6 \otimes \mathcal{U}_6 \otimes \mathcal{U}_3, \quad (12)$$

where (i)  $\mathcal{U}_6$  is given by equation (3), and  $\mathcal{U}_3$ , the transformation appropriate to three-fold symmetry, is defined by:

$$\mathcal{U}_3 = \frac{1}{\sqrt{3}} \begin{bmatrix} 1 & 1 & 1 \\ 1 & \omega & \omega^2 \\ 1 & \omega^2 & \omega^4 \end{bmatrix} = \frac{1}{\sqrt{3}} \begin{bmatrix} 1 & 1 & 1 \\ 1 & \omega & \omega^* \\ 1 & \omega^* & \omega \end{bmatrix}, \quad \omega = e^{i2\pi/3}. \quad (13)$$

When this done, the Hamiltonian takes the block diagonal form:

$$\mathcal{H}_2(\mathcal{J}_z = +1) = -\frac{1}{4} [H_1 \otimes H_2 \otimes H_3 \otimes H_4 \otimes H_5 \otimes H_6 \otimes H_7], \quad (14)$$

where:

$$H_1 = \begin{bmatrix} -4\alpha + 2\beta & 2\alpha + 2\gamma & 2\sqrt{2}\beta \\ 2\alpha + 2\gamma & -2\beta & 2\sqrt{2}\alpha \\ 2\sqrt{2}\beta & 2\sqrt{2}\alpha & -4\gamma \end{bmatrix} \begin{bmatrix} |1'\rangle \\ |7'\rangle \\ |13'\rangle \end{bmatrix}, \quad (15)$$

$$H_2 = \begin{bmatrix} -4\alpha + 2\beta & z_1 \\ z_1^* & -5\beta \end{bmatrix} \begin{bmatrix} |2'\rangle \\ |8'\rangle \end{bmatrix}, \quad z_1 = \frac{3}{2} + i\frac{\sqrt{3}}{2}, \quad (16)$$

$$H_3 = \begin{bmatrix} -4\alpha - \beta & (\alpha - 2\gamma)z_2 & \sqrt{2}\beta z_2^* \\ (\alpha - 2\gamma)z_2^* & -5\beta & \sqrt{2}\alpha z_2 \\ \sqrt{2}\beta z_2 & \sqrt{2}\alpha z_2^* & -4\gamma \end{bmatrix} \begin{bmatrix} |3'\rangle \\ |9'\rangle \\ |14'\rangle \end{bmatrix}, \quad z_2 = \frac{1}{2} + i\frac{\sqrt{3}}{2}, \quad (17)$$

$$H_4 = [-4\alpha + 2\beta]|4'\rangle \quad (\text{singlet}), \quad (18)$$

$$H_5 = \begin{bmatrix} -4\alpha - \beta & (\alpha - 2\gamma)z_2^* & \sqrt{2}\beta z_2 \\ (\alpha - 2\gamma)z_2 & -5\beta & \sqrt{2}\alpha z_2^* \\ \sqrt{2}\beta z_2^* & \sqrt{2}\alpha z_2 & -4\gamma \end{bmatrix} \begin{bmatrix} |5'\rangle \\ |11'\rangle \\ |15'\rangle \end{bmatrix}, \quad z_2 = \frac{1}{2} + i\frac{\sqrt{3}}{2}, \quad (19)$$

$$H_6 = \begin{bmatrix} -4\alpha + \beta & z_1^* \\ z_1 & -5\beta \end{bmatrix} \begin{bmatrix} |6'\rangle \\ |12'\rangle \end{bmatrix}, \quad z_1 = \frac{3}{2} + i\frac{\sqrt{3}}{2}, \quad (20)$$

$$H_7 = [-2\beta]|10'\rangle \quad (\text{singlet}). \quad (21)$$

Note that all the wavefunctions have been embellished with a dash, to indicate that they are the wavefunctions obtained after the unitary transformation of equation (11) has been applied.

Equations (15)–(21) are identical with those of [3], except for an almost complete relabelling of the wave-functions. In passing, we also note that  $H_5 = H_3^*$ , and  $H_6 = H_2^*$ , so that in practice, it is only necessary to diagonalise a  $2 \times 2$  and two  $3 \times 3$  matrices.

From an examination of equation (15), it is evident that the three wavefunctions of  $H_1$  are mixtures of three symmetric wavefunctions, all characterised by the ‘wave-vector’  $k_r = 0$ . Similarly, the two eigenfunctions of  $H_2$  are characterised by two spin-waves with  $k_r = (2\pi/6a)$ . But note that vectors from the third group  $|13'\rangle$ – $|15'\rangle$  are excluded because this set of eigenvectors cannot support  $k_r = (2\pi/6a)$  spin-waves. However this is not the case for the eigenvalues of  $H_3$ , where admixing occurs between three wavefunctions, all characterised by  $k_r = 2(2\pi/6a)$ . Very similar arguments can be advanced for  $H_5$  ( $k_r = 4(2\pi/6a)$ ) and  $H_6$  ( $k_r = 5(2\pi/6a)$ ).

But perhaps the greatest surprise lies in the observation that the eigenfunctions of  $H_4$  and  $H_7$  are not admixed but are singlets. The wavefunctions associated with these eigenvalues are  $|4'\rangle$  and  $|10'\rangle$ , respectively, both of which are characterised by phase changes of  $e^{i\pi}$  between neighbouring wavefunctions. So the possibility for interference exists. However, note that the three wave functions  $|13'\rangle$ – $|15'\rangle$  cannot be admixed into  $|4'\rangle$  and  $|10'\rangle$ , because the former cannot support spin-waves with phase differences  $e^{i\pi}$ .

Finally, we state without proof that the above treatment can be extended to the  $20 \times 20$  matrix associated with  $\mathcal{J}_z = 0$ . In this case three spin-waves are involved. In summary therefore, the nuclear excitations of the  ${}^1_1H$  spins in the benzene ring can be described in terms of spin-waves, and/or mixtures of spin-waves with a common wave-vector  $k_r$ .

#### 4. MQ-NMR and nuclear spin dynamics

A full description of  $\Delta m = \pm 4$  and  $\pm 5$  MQ-NMR experiments on the benzene ring has already been given in detail in [3], where it is shown that there is excellent agreement between theory and experiment. In this section, we stress that MQ-NMR experiments can be used to probe the nuclear spin-dynamics of the benzene ring.

In the past, MQ-NMR experiments have been described largely in terms of simple single-spin Zeeman energy level diagrams, implicitly neglecting spin-spin interactions. However, for the benzene ring, the entire description of MQ-NMR experiments can be re-couched in terms of collective nuclear spin-wave states. This provides a deeper description, enriched by the knowledge of the specific eigenvectors and the spin-wave excitations involved. For example,  $\Delta m = +4$  experiments on the benzene ring target indirect transitions from  $\mathcal{J}_z = -3 \rightarrow +1$  and  $\mathcal{J}_z = -2 \rightarrow +2$ . The first set involves transitions from a fully symmetric  $\mathcal{J}_z = -3$  collective spin-wave, with  $k_r = 0$ , to a dual mixed spin-wave state characterised by  $\mathcal{J}_z = +1$ . The second set however involves transitions from one spin wave state to another. For the latter, the only allowed transitions are between spin-wave states with the same wave-vector  $k_r = 2\pi/6a$ . These arguments are easily extended to  $\Delta m = +3$  etc., experiments etc.

#### 5. Conclusions

In this paper, it has been shown that the DFT can be used to advantage in the diagonalization of the nuclear Hamiltonian for the benzene ring. Further, the transformed wave-functions allow parallels to be drawn between Bloch's theorem and nuclear spin-wave states. In particular, it has been shown that (i) the nuclear wave-functions of the benzene ring, can be understood in terms of either singular or mixed spin-wave states, and (ii) it is possible to identify those spin waves states which are targeted in a given MQ-NMR experiment. But perhaps the most striking conclusion of all is that MQ-NMR experiments, performed at room temperature, can be used study the nuclear spin-dynamics  $\sim 1$  kHz ( $\sim 10^{-7}$  K) of the benzene ring. Normally, in the study of weak energy excitations, very low temperatures are essential. But the high resolution ( $\sim 1$  Hz) plus the high selectivity of the MQ-NMR experiment, allows weak collective nuclear excitations to be examined at room-temperature.

#### References

- [1] G.J. Bowden and T. Heseltine, *J. Math. Chem.* 19 (1996) 353.
- [2] G.J. Bowden, T. Heseltine and M.J. Prandolini, *J. Math. Chem.* 19 (1996) 365.
- [3] G.J. Bowden, T. Heseltine and M.J. Prandolini, *J. Math. Chem.* 20 (1996) 285.
- [4] W.S. Warren, S. Sinton, D.P. Weitekamp and A. Pines, *Phys. Rev. Lett.* 43 (1979) 1791.
- [5] W.S. Warren, Ph.D. thesis, Berkley (1980).
- [6] W.S. Warren and A. Pines, *J. Chem. Phys.* 74 (1981) 2808.
- [7] W.S. Warren and A. Pines, *J. Am. Chem. Soc.* 103 (1981) 1613.

- [8] A.M. Panich, *J. Magn. Reson.* A116 (1995) 113.
- [9] N.W. Ashcroft and N.D. Mermin, *Solid State Physics* (Holt Sanders, 1981) p. 704.
- [10] R.J. Elliott and A.F. Gibson, *An Introduction to Solid State Physics and its Applications* (Macmillan Press, 1974).
- [11] M. Tinkham, *Group Theory and Quantum Mechanics* (McGraw Hill, 1964).
- [12] D.E. Knuth, *The Art of Computer Programming*, Vol. 2 (Addison-Wesley, 1981).
- [13] J.W. Cooley and J.W. Tukey, *Math. Comp.* 19 (1965) 297.