Deuterium NQR Spectra: Dipolar Interaction Between Two Quadrupolar Nuclei

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Z. Naturforsch. **40 a,** 355 – 360 (1985); received February 6, 1985

Dedicated to Alarich Weiss on the Occasion of his 60th Birthday

The pure quadrupole spectra of dipolar coupled nuclei in solids contain weak combination and difference bands, usually referred to as DTQR transitions, together with the normal (e.g. allowed) lines. The forbidden lines contain useful information about the relative orientations of the field gradient tensors at the coupled nuclei. If the coupled sites are crystallographically equivalent, the symmetry imposes constraints upon the relative orientations of the tensors, and the spectra contain information which can be used in the assignment of spectra. It is shown how some information may be obtained even in the absence of symmetry constraints.

The purpose of this note is the generalization of previous theoretical work, notably by Edmonds and White, to the case of two coupled nuclei of spin $I = 1$ and with *arbitrarily* oriented field gradient tensors. The theory is given in a computationally convenient form, and example spectra are given for comparison with recent experimental work in this laboratory.

Introduction

The effect of dipole coupling on the fine structure of pure quadrupole spectra in solids has been considered previously on many occasions [1]. With the development of high sensitivity double resonance methods, many features of such spectra for nuclei such as deuterium have become experimentally accessible, and Edmonds and co-workers [2] have considered the normally forbidden transitions which arise in this way in several publications. Groups such as $-NH_2$ and $-OH_2$ were treated in this previous work, and Poplett and Smith [3], and Day, Hadipour and Ragle [4], [5] have discussed the use of such spectra as indicators of structural features. To indicate the complexity of the spectrum of a single pair of deuterons in intermolecular contact in a solid, we show in Fig. 1 the entire calculated spectrum of a pair of imido (N–D) groups separated (as in anhydrous imidazolidone, vide infra) by 2.70 Å, with the intensities plotted on a logarithmic scale. The lines in the combination band region, here between 297 and 330 kHz, are probably the easiest of the forbidden lines to observe, since they are relatively far from both the proton dipolar absorption and the much stronger normal bands. Further comments on this example are given below.

The theory given by Edmonds and White and expounded in detail by Poplett pertains to a situation

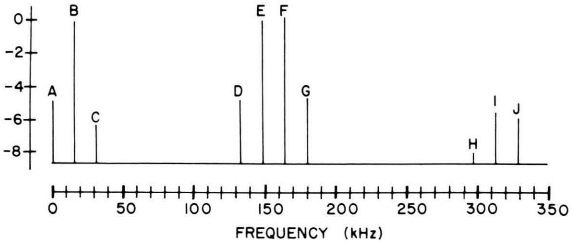

Fig. 1. Example pure quadrupole spectrum of two weakly-coupled deuterons, showing forbidden and allowed transitions on a logarithmic intensity scale. The example considered corresponds to the 2.70 A contact in anhydrous imidazolidone between HN (x, y, z) and HN ($1.25-x, 1.25-y, -z$) and to a tensor orientation in which the major (z) principal axis is along the N-H axis and the minor (y) axis is perpendicular to the C(1)–N–H plane. This corresponds to 0° in Figure 4. The spectrum contains 36 transitions, of which B, E and F are the normal lines v_0, v_- and v_+ respectively. Their fine structure is not evident on this frequency scale, but each is a near superposition of 8 transitions with a frequency spread of the order of 0.5 – 0.7 kHz. The lines H–J are considered in more detail in Fig. 4, in which the intensities are shown on a scale linear in the square modulus of the transition moment. The multiplicities of the other lines are A(3), C(1), D(2), G(2), H(1), I(2), J(1).

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in which special interrelations exist between the field gradient tensors at the two coupled nuclei, in the sense that the relative orientations of the two tensors could be characterized by one, or possibly two angles. We report here the generalization of this theory to arbitrary orientation of the two tensors. The theory is cast into convenient form for machine computation, and we discuss the simulation of spectra obtained for several molecular crystals in this laboratory.

Theory

Although the theory of the dipolar interaction between quadrupolar nuclei is straighforward and well known, we wish to offer a computationally convenient formulation for the simulation of DTQR spectra. We work with three coordinate systems, the *orthogonalized* crystal coordinate system, and two local systems, also orthogonal, at the crystal sites of the two coupled nuclei. The latter are taken to be the principal axis systems of the field gradient tensor of the quadrupole interaction at these sites. The Hamiltonian, including the individual quadrupole coupling term at each site and the dipolar interaction between them, is often written as follows:

$$\hat{H}_{\mathrm{T}} = \hat{H}_{\mathrm{Q}} + \hat{H}_{\mathrm{D}}\,,$$

$$\begin{aligned}\hat{H}_{\mathrm{Q}} = e^2 q_1 Q_{\mathrm{D}}\,(3\,\hat{I}_z'^{2}(1) \\ + \eta\,(\hat{I}_x'^{2}(1) - \hat{I}_y'^{2}(1)) - 2)/4 \\ + \text{similar term for site (2)}\,,\end{aligned}$$

$$\hat{H}_{\mathrm{D}} = d\,\{\hat{I}(1)\cdot\hat{I}(2) - 3\,\hat{I}(1)\cdot\boldsymbol{r}_{12}\,(\hat{I}(2)\cdot\boldsymbol{r}_{12}\}\,,$$

$$\hat{H}_{\mathrm{RF}} = \gamma\hbar\,\{\hat{I}(1)\cdot\boldsymbol{H}(1) + \hat{I}(2)\cdot\boldsymbol{H}(2)\}\,,$$

with $d = \gamma^2\hbar^2/r_{12}^3$ and where $\boldsymbol{r}_{12}$ is a unit vector along the line connecting the two sites. In the expressions for $\hat{H}_{\mathrm{Q}}$, $I'(1)$ and $I'(2)$ are expressed in their respective local (primed) principal axis systems, but in the expression given for $\hat{H}_{\mathrm{D}}$, $I(1)$ and $I(2)$ are in a common coordinate system. Let $\{\boldsymbol{e}_j^{(1)}\}$ and $\{\boldsymbol{e}_j^{(2)}\}$ be unit vectors which define the local systems at sites 1 and 2, expressed in any convenient common system, usually the crystal system, and let α be the matrix of direction cosines $\alpha_{ij} = \langle \boldsymbol{e}_i^{(2)} | \boldsymbol{e}_j^{(1)} \rangle$. Because α is constrained to unitarity, the 9 direction cosines may be given in terms of the three angles interrelating the two systems, customarily a set of Euler angles. In terms of this matrix, the dipolar Hamiltonian $\hat{H}_{\mathrm{D}}$ is

$$\hat{H}_{\mathrm{D}} = d\,\{\hat{I}'(1) - 3\,(\boldsymbol{r}_{12}\cdot\hat{I}'(1))\,\boldsymbol{r}_{12}\}\cdot\alpha^{\mathrm{T}}\,\hat{I}'(2)\,,$$

where the prime (′) again refers to the local systems and α^{T} is the transpose of α.

If E1 and E2 are the matrices the columns of which are the vectors $\{\boldsymbol{e}_i^{(1)}\}$ and $\{\boldsymbol{e}_j^{(2)}\}$ respectively, then α is computed as $\mathrm{E1}^{\mathrm{T}}\,\mathrm{E2}$. Defining two additional matrices

$$\beta = d\,\{1 - 3\;(\mathrm{E1}^{\mathrm{T}}\boldsymbol{r}_{12})\,(\mathrm{E1}^{\mathrm{T}}\boldsymbol{r}_{12})^{\mathrm{T}}\}$$

(the column-row product) and

$$G = \alpha\,\beta\,,$$

the dipolar interaction is

$$\hat{H}_{\mathrm{D}} = \hat{I}'(2)\;G\;\hat{I}'(1)\,,$$

where the prime has the same significance as above. In this notation, the coefficients relating the applied RF perturbation at sites 1 and 2 in the local systems are

$$\langle H_i'(1)\,H_j'(1)\rangle = (h_{\mathrm{RF}}^2/3)\,\delta_{ij}\,, \tag{a}$$

$$\langle H_i'(1)\,H_j'(2)\rangle = (h_{\mathrm{RF}}^2/3)\,\alpha_{ij}\,, \tag{b}$$

where the averages denoted by $\langle\ldots\rangle$ are over a random distribution of crystallite axes in a polycrystalline sample, as explained for the special case by Edmonds and White, and where h_{RF} is the magnitude of the applied RF magnetic field. A convenient computation scheme is therefore the diagonalization of $\hat{H}^{\mathrm{T}}$, the transformation of $\hat{H}_{\mathrm{RF}}$ to this basis, and the subsequent assembly of the coefficients (a), (b) to yield the square moduli of the associated transition moments. The actual coding involved is minimal, and we would be pleased to furnish to CDC FORTRAN IV listing which utilizes the EISPACK routines to diagonalize the 9×9 complex matrices involved in the arithmetic and computes relative intensities from given crystal data. The only detail which requires special attention is the maintainance of suitable precision for the computation of the intensities of the forbidden transitions, which are computed in some cases as rather small differences between large quantities.

Additional Comments and Examples

The major impediment to the full use of these forbidden transitions as a structural tool for hydrogen is the fact that while the crystal structure is often known with reasonable precision, the directions of the principal axes of the field gradient are not known unless the site itself lies on a position of special symmetry. Furthermore, for intermolecular contacts, which are frequently longer than 2 Å, it is often the case that not all the dipolar structure is resolvable at this stage in the development of the experimental technology. There are however several ways in which the simulated spectra can make useful contact with experiment. If sites lie at positions of special symmetry, this symmetry yields some knowledge of the tensor directions and spectra may be calculated directly. For equivalent nuclei, the crystal symmetry operations control the relationship between the two systems. One may then either use the simulated spectra to assign peaks in complex spectra by making chemically reasonable assumptions about axis directions, or use the observed intensities to gain some information about the orientation of the field gradient tensor with respect to the molecular frame. As an example, one may be quite confident that the major principal axis direction for deuterium involved in a single strong chemical bond will lie within a few degrees of that bond direction. For functional groups, the field gradient directions of which have been determined for a single specific case, one may also extrapolate to similar chemical environments.

The first example which we consider is the case of catechol. The material is a molecular solid exhibiting a complex network of hydrogen bonds, and Day, Hadipour, and Ragle [4] have used the DTQR spectrum to assign crystallographic sites to observed normal NQR lines in the (O)-deuterated solid. In this work, the authors used the theory of Edmonds and White as a qualitative guide, and erroneously concluded that a weak observed DTQR line was symmetry forbidden on this basis. When the theory is properly generalized here to include all parameters which characterize the relative orientation of interacting hydroxyl deuterons, a satisfactory fit of theory to experiment is achieved without ad hoc assumptions about possible changes in structure. The experimental and theoretical spectra are shown in Fig. 2, taken under conditions in which h_{RF} in the experimental spectrum (4) is nearly constant across the range of frequencies here encompassed. The simulated spectrum was computed by assuming that the major principal axis of the field gradient tensor is parallel to the O−D axis for both crystal sites. It was also assumed that the minor principal axis of intermediate length (the "y" axis in conventional NQR nomenclature) for each tensor was perpendicular to the plane defined by the O−D group and the carbon atom to which it is bonded. Both these assumptions have been discussed previously [6] and do not appear to be in question. The line pairing of Day, Hadipour and Ragle has been used in Figure 2. If another possible line pairing is assumed, or if a substantially different tensor orientation is chosen, the simulated spectrum is very different from the experimentally observed one. A specific example of this is also shown in Figure 2.

A second example is the DTQR spectrum of phenylphosphonic acid-(O)-d_2 (PPA), shown in Figure 3. This was recently obtained by Day, Hadipour and Ragle [5] as an adjunct to structural work on cocrystals of catechol, PPA and pyridine, and the spectrum was used to establish line pairings for the four peaks observed in the allowed spectrum. This assignment turns on a simple feature of the DTQR spectrum, namely appearance of a combination band arising from interaction between symmetry-related $(H(1)-H'(1))$ nuclei. Several other features of the spectrum are noteworthy, namely the appearance of the $2\nu_+$ line near 270 kHz, the intensity ratio of the doublet at 255, 260 kHz, and the

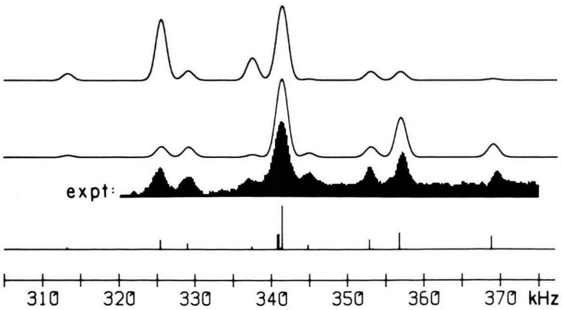

Fig. 2. Computed and observed DTQR spectra for catechol at 77 K. The simulated spectra are obtained by convolution of the stick spectra with a Gaussian of 1 kHz rms deviation. The simulated spectrum labelled 'a' corresponds to the frequency assignments of [4] and with the y-axes of the field gradient tensors taken to be perpendicular to the C−O−H planes for both sites, in agreement with the calculations of [6]. Spectrum 'b' corresponds to the same frequency assignments, but with the x-axes of the tensors perpendicular to the C−O−H planes for the two crystallographic sites.

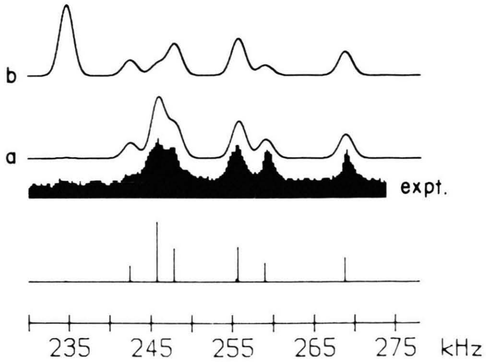

Fig. 3. Computed and observed DTQR spectra for phenylphosphonic acid at 77 K. The simulated spectra are obtained by convolution of the stick spectra with a Gaussian of 1.2 kHz rms deviation. The simulated spectrum labelled 'a' corresponds to the frequency assignments of [5] and has the y-axes of the field gradient tensors rotated 15 degrees away from perpendicularity with the P–O–H planes for both sites by rotation about the O–H bond. The O–H vector is presumed to be the z-axis of the tensor. Spectrum 'b' corresponds to the same frequency assignments, but with the tensor of site 1 rotated through an angle of 40 degrees about O–H1, while the site 2 tensor has its y-axis perpendicular to the P–O–H2 plane. The latter spectrum is included to illustrate the sorts of changes which occur upon rotation, not to imply that its particular orientation is otherwise significant.

Table 1. Comparison of forbidden line intensities for two orientations of the deuterium field gradient tensor in imidazolidone. Columns 1 and 2 are computed from a geometry in which the z axis is along N–H and the y axis is perpendicular to the C1–N–H plane. Columns 3 and 4 are computed from the geometry which is obtained by 60-degree rotation of the tensor about the N–H axis. Both orientations give agreement with the observed DTQR spectrum in the combination region around 300 kHz.

1[a] Frequency	2[b] Intensity	3[a] Frequency	4[b] Intensity	Origin
132.88	1.61 E-5	132.78	5.44 E-5	$\vert yz\rangle, \vert zy\rangle \rightarrow \vert xx\rangle$
133.02	6.16 E-6	133.14	1.23 E-4	
179.67	9.77 E-6	179.87	1.51 E-4	$\vert xz\rangle, \vert zx\rangle \rightarrow \vert yy\rangle$
180.13	1.99 E-5	179.94	4.08 E-5	
297.20	1.01 E-8	297.20	1.12 E-9	$\vert zz\rangle \rightarrow \vert xx\rangle$
312.72	2.40 E-6	312.72	2.15 E-6	$\vert zz\rangle \rightarrow \vert xy\rangle, \vert yx\rangle$
312.98	3.03 E-6	312.98	2.56 E-6	
328.50	1.35 E-6	328.50	1.68 E-6	$\vert zz\rangle \rightarrow \vert yy\rangle$

[a] Computed frequency in kHz.
[b] Relative values. On this scale, the allowed transitions have an intensity in the neighborhood of unity.

obviously multiple structure of the square-topped peak at around 245 kHz. Simulations of this spectrum are shown in Fig. 3 for various orientations of the field gradient tensors at the two sites. A reasonably satisfactory match to the observed spectrum is obtained for the line assignment of Day, Hadipour and Ragle and with the y-axis of the field gradient tensor at both sites perpendicular to the plane defined by the phosphorous, oxygen and hydrogen atoms. Intensities of certain of the DTQR lines are very sensitive to geometry (see Fig. 1) and in this regard it should be noted that the proton positions in the structure of Weakley are probably not very accurately known; this inaccuracy will be reflected in the field gradient tensor orientations because they have been assumed to be dictated by the local geometry of the molecule. Slight (+/− 15 degree) adjustments of the angular orientation of the field gradient principal axis system would probably considerably improve the fit to the experimental spectrum.

As a third example, we consider the case of the imino deuterons in anhydrous imidazolidone-(N,N′)-d_2. The structure contains a single imido site, and the dominant contact is an intermolecular one at a distance of 2.70 A. The spectrum associated with this site has been discussed by Day, Hadipour and Ragle [7] in the context of the hydrogen bonding present, and it is in a case such as this that a reasonably precise determination of the field gradient tensor directions can be established from the DTQR spectrum. Figure 4 shows the behavior of the intensities of the four DTQR lines as the field gradient tensor is rotated about its z-axis, assumed to be collinear with the N–H bond. The observed spectrum consists of two peaks, the transitions (2, 3) $|zz\rangle \rightarrow |xy\rangle, |yy\rangle$ (unresolved, computed splitting ca. 270 Hz), and the transition (4) $|zz\rangle \rightarrow |yy\rangle$, with the transition (1) $|zz\rangle \rightarrow |xx\rangle$ unobserved. The transitions are identified by their frequencies, and the intensity distribution is consistent with an orientation in which the y-axis of the field gradient tensor is nearly perpendicular to the C–N–H plane. It can be seen from the figure that there is also a second orientation which is consistent with experiment in which the tensor y-axis is tipped about 60 degrees from this plane. Table 1 shows the intensity distributions for the forbidden lines computed for these two orientations. It is possible that this ambiguity could be resolved by observation of

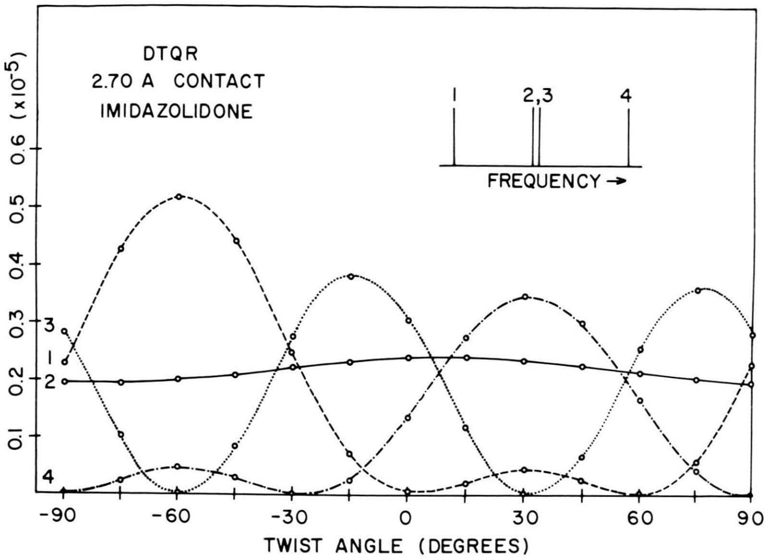

Fig. 4. Plot of the intensities of the high-frequency bands in a pure quadrupole spectrum of two weakly-coupled deuterons. The example corresponds to the same pair as illustrated in Fig. 1 for anhydrous imidazolidone, but with the two symmetry-related field gradient tensors rotated about the N–H axis by the amount indicated on the abscissa. The ordinate is linear in the square modulus of the transition moment, and the allowed lines have transition moments of ca. unity on this scale. The two lines 2, 3 are not resolved in the experimental spectra of [7].

other forbidden transitions, particularly those at ca. 133 kHz and 180 kHz; in the second case these transitions, especially those at 133 kHz, are much stronger (two to three orders of magnitude) than in the first case. The lines in question are unfortunately only visible as shoulders on the allowed spectrum, and we are not able to make any confident assessment of their intensities. A second problem has to do with the assessment of the intensity of the DTQR transition $|zz\rangle \rightarrow |xx\rangle$. In this compound, its calculated position lies within the dipolar absorption edge of the protons in the sample at the RF intensities necessary to observe DTQR transitions, and we have no way of knowing the extent to which it is masked by this feature of the spectrum.

Conclusion

We have presented a computationally convenient form of the theory of the dipolar interaction between two quadrupolar coupled nuclei at zero field for the case of arbitrarily oriented tensor axes, as well as several simple examples of spectra simulated using this theory. The simulated spectra have been plotted as frequency versus the square modulus of the transition moment computed from first order time-dependent perturbation theory. As previously emphasized by Edmonds and White, the observed spectral intensities derive from a double-resonance experiment, the response of which is often not a particularly linear function of the square modulus of the transition moment. In addition, DTQR spectra of materials in which more than two types of short contacts are present were computed by the *superposition* of the spectra of pairs. This is justified on the basis of the two-body form of the dipole interaction and the smallness of the dipolar coupling itself. Spectra simulated in this way do give a reasonable qualitative account of the observed spectra, and it appears that deductions concerning tensor orientation are in good accord with chemical expectations for the case of catechol, in which intermolecular hydrogen bonding is relatively weak and the tensor directions are known with some certainty on other grounds. In the case of phenylphosphonic acid, in which the deuteron coupling constants show that the local electronic structure is substantially more strongly perturbed by the hydrogen bonding, comparison between experiment and these simulations suggests that the directions of the x and y axes of the field gradient tensor at deuterium are nevertheless the same, e.g. with the y axis roughly perpendicular to the P–O–H plane.

Acknowledgements

We would like to acknowledge the contributions made to this work by Dr. R. K. McMullan, Brookhaven National Laboratory and Prof. R. O. Day of this Department. The work was supported by NSF Grant CHE-8111431.

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