Determination of the Geminal Coupling Constants in 1-Bromo-2-chloroethane. A Novel Use of Double Quantum Transitions

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Summary The two geminal proton–proton coupling constants in 1-bromo-2-chloroethane have been determined by making use of the observation of double quantum transitions.

DOUBLE QUANTUM TRANSITIONS (DQT) have been used as an aid in the analysis of n.m.r. spectra, principally to determine the relative signs of coupling constants.[1–4] We now report that, with the help of DQT, it is possible to determine all the coupling constants in a spectrum which otherwise could be only partially analysed.

The Figure (a) shows the normal 100 MHz spectrum of a 20% w/w solution of 1-bromo-2-chloroethane in CCl_4. This is an AA′BB′ system and the spectrum shows 20 lines. It is a straightforward matter[5] to obtain from it the parameters δ ($=\nu_A - \nu_B$), L ($=J_{AB} - J'_{AB}$), M ($=J_{AA} - J_{BB}$) and N ($=J_{AB} + J'_{AB}$); but K ($=J_{AA} + J_{BB}$) cannot be determined as it only affects one eigenvalue ($3s'_0$); and the four transitions 5, 8, 5′, and 8′ involving this eigenvalue are too weak to be observed† (for notation and details, see ref. 5a).

As part of a wider study of multiple quantum transitions, we have also observed the spectrum under steadily increasing values of the irradiating field H_1 and have found 12 out of the 16 possible DQT lines, and 2 out of 4 possible triple quantum lines (as well as a pair of single quantum combination bands 1c and 1′c) (Figure, b). Of the DQT lines, two, namely 5d and 12d (in the notation of ref. 1a), involve the stationary state $3s'_0$, whose energy could not be obtained from the observed single quantum lines. As these two sharp DQT lines have been unambiguously determined, the problem is in principle solved, and K can be determined.

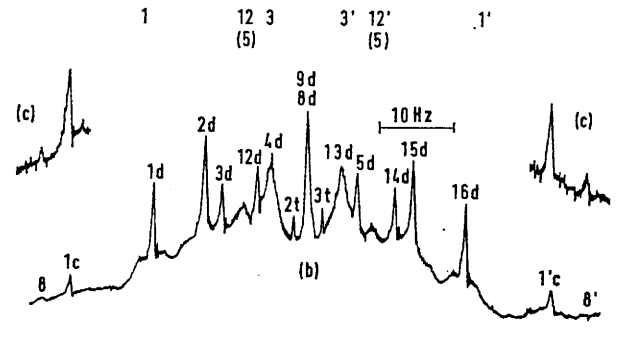

FIGURE. ^{1}H *N.m.r. spectra of* 1-*bromo*-2-*chloroethane at* 100 MHz (a) *Normal conditions*; (b) *high* H_1 *showing multiple quantum and combination lines*; (c) *high* H_1 *and high sensitivity, showing very weak outer lines.*

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† 5 and 5′ are overlapped by 12′ and 12.

Expressed in terms of transition frequencies rather than eigenvalues, the frequency of the DQT is given by

$$12\mathrm{d} = \tfrac{1}{2}(3 + 5') = \tfrac{1}{2}(1' + 8).$$

In this way, the positions of the weak lines 5, 5′, 8, and 8′ were deduced. To conclude the problem, we chose to use the iterative computer programme LAME,[6] including these last four quantities in the input data. The final results were: $\delta = 0{\cdot}218$ p.p.m., $K = -20{\cdot}76$, $L = 4{\cdot}80$, $M = 1{\cdot}00$, $N = 16{\cdot}12$; $J_{AA} = -9{\cdot}88$, $J_{BB} = -10{\cdot}88$, $J_{AB} = 10{\cdot}46$, $J'_{AB} = 5{\cdot}66$ (all $\pm 0{\cdot}01$) Hz. The values of δ, L, M, and N are in good agreement with previous results.[7]

The positions of the remaining DQT and triple quantum lines agreed within experimental error with the positions predicted from these parameters. However, the positions of the crucial DQT lines 5d and 12d shifted by up to 0·2 Hz as H_1 was increased; this shift is theoretically predicted,[8] and should be borne in mind when the present method is being used for the accurate determination of coupling constants. At high H_1 *and* very high sensitivity, it was even possible to observe at their predicted positions the transitions 8 and 8′ (Figure, c); as their calculated intensity is only 0·002 on a scale where that of the whole spectrum is 32, it is clear that in many parallel cases the corresponding lines may be unobservable even under such extreme instrumental conditions.

This type of situation is characteristic of a wide variety of cyclic and acyclic molecules containing a $-CH_2-CH_2-$ fragment. Furthermore, the structural implications of geminal coupling constants are being increasingly recognized.[9]

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