Determination of Deuteron Quadrupole Coupling Constant in the Liquid State

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Summary A method of determining deuteron quadrupole coupling constants for deuterium directly bonded to carbon in molecules in the liquid state is described, which involves measurements of the deuteron spin–lattice relaxation time and that of the ^{13}C nucleus in the undeuteriated molecule; values of 227 and 186 MHz are obtained for phenyl[$^2H_1$]acetylene and [$^2H_6$]benzene, respectively.

THE determination of deuterium quadrupole coupling constants (e^2Qq_{zz}/h) in organic molecules in the liquid phase is available, in principle from the studies of the spin–lattice relaxation of the deuteron, a process which is completely dominated by the quadrupole mechanism. Equation (1) shows that the relaxation time, T^Q, is related to the quadrupole coupling constant (e^2Qq_{zz}/h) through $f(\Omega,D)$. The elements of Ω are geometric factors relating the rotational diffusion axes to the direction of q_{zz}, the field gradient at the deuteron, which is assumed to be axially symmetric.[2] **D** is the rotational diffusion tensor. If rotational diffusion is isotropic, $f(\Omega,\mathbf{D})$ can be replaced by a single correlation time, τ_C. A number of workers[3,4] have attempted to determine quadrupole coupling constants by assuming isotropy of rotational diffusion and estimating

τ_C from the intramolecular dipole–dipole spin–lattice relaxation times (T_1^{DD}) for protons. Assink and Jonas[3] have pointed out that this procedure is only valid in those rare cases in which the sole intramolecular dipole–dipole interactions are between pairs of protons, the internuclear vectors for which are parallel with q_{zz}. In other cases the assumption of isotropy may lead to serious errors. Furthermore, the evaluation of the intramolecular contribution to T_1^{DD} requires a tedious and error-prone extrapolation of the observed T_1's to infinite dilution in magnetically inert solvents. We now show that the problem of anisotropic rotational diffusion can always be avoided by combining $T_1^Q(^2H)$ with the ^{13}C dipole relaxation time $T_1^{DD}(^{13}C)$ for the same carbon atom in the undeuteriated molecule to which the deuteron is attached in the deuteriated species. In this situation the ^{13}C–H internuclear vector is necessarily colinear with q_{zz} and $g(\Omega,\mathbf{D})$ in equation (2)[1,5] is identical with $f(\Omega,\mathbf{D})$ in equation (1). The quadrupole coupling constant is then given by equation (3) in which r_{CH} is the C–H bond length in Å. We now apply equation (3) in two

$$1/T_1^Q(^2H) = \tfrac{3}{8}\,(e^2Qq_{zz}/\hbar)^2 \cdot f(\Omega.\mathbf{D}) \qquad (1)$$

$$1/T_1^{DD}(^{13}C) = (\gamma_C^2\gamma_H^2\hbar^2/r_{CH}^6) \cdot g(\Omega,\mathbf{D}) \qquad (2)$$

$$(e^2Qq_{zz}/h) = 49{\cdot}3\, r_{CH}^{-3}\,(T_1^{DD}/T_1^Q)^{\frac{1}{2}}\text{-(kHz)} \qquad (3)$$

systems for which fairly reliable estimates of the deuteron quadrupole coupling constants are available from other sources.

T_1^Q for phenyl[$^2H_1$]acetylene is 0·28 ± 0·01 at 299 K[6] and, at this temperature, we find T_1^{DD} for the β-carbon atom in degassed phenylacetylene to be 8·2 ± 0·1 s (at this temperature the nuclear Overhauser enhancement is 1·98, so that $T_1^{obs} = T_1^{DD}$). With r_{CH} = 1·056 Å,[7] the C–H bond length in acetylene, equation (3) gives 227 ± 4 kHz for the deuteron quadrupole coupling constant. This value may be compared with 215 ± 5 obtained from wide-line n.m.r. studies[8] on polycrystalline phenyl[$^2H_1$]acetylene at 199 K and 230 ± 14 for p-di[$^2H_2$]ethynylbenzene in CD_3CN at 299 K.[3] This latter value was obtained by using proton relaxation times and is a case in which the H–H internuclear vectors are parallel with q_{zz}.

The value for $T_1^{DD}(^{13}C)$ for degassed benzene at 311 K is reported[9] to be 37 s and we have confirmed this value. Interpolation of the T_1^Q *vs.* temprature data for [$^2H_6$]benzene reported by Powles *et al.*,[10] gives T_1^Q = 1·6 s at this temperature and using (3) a deuteron quadrupole coupling constant of 186 kHz is calculated. This value may be compared with 193 ± 3 from studies in the nematic phase,[11] 186·6 ± 1·6 from deteuron magnetic resonance of single crystals,[12] and 200 ± 10 using proton and deuteron spin–lattice relxation times.[10] Other pertinent values are 180 for chloro[$^2H_5$]benzene (low temperature, wide-line n.m.r.),[13] 181 ± 10 for p-chloro[$^2H_1$]benzene from proton and deuteron spin-lattice relaxation times (this is another case in which r_{CH} and q_{zz} are parallel.)[3] Finally, Ellis and Bjorkstam[14] have performed a very careful wide-line n.m.r. study of oriented single crystals of perdeuterioanthracene and have found the value of 181 ± 3 kHz for all three types of deuterons.

If $T_1^{DD}(^{13}C)$ and $T_1^Q(D)$ can be determined with an accuracy of ±5% and r_{CH} is accurate to ±0·01 Å, the propagated error in the quadrupole coupling constant is ±4·5%. The great advantage of the method is that it requires no knowledge of the rotational diffusion tensor and no knowledge of molecule geometry other than r_{CH}.

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