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The Deuterium Quadrupole Coupling Constants of Di- and Trihalomethanes

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There have recently been published a number of papers reporting the deuterium quadrupole coupling constants (QCC) of small molecules dissolved in liquid-crystalline media (*1–5*). The results presented show, in many instances, wide variations in QCC values determined by different groups. These differences can be mainly attributed to the presence of different solvent–solute interactions in different liquid-crystal phases. Other causes of the range of values found arise from the difficulty in choosing appropriate bond lengths and making vibrational corrections to the dipolar couplings. Such uncertainties have led to some puzzling anomalies. For example, with the deuterohalomethanes, tribromomethane appears to have a considerably larger QCC than either trichloromethane or triiodomethane. These results have prompted us to determine the QCC values for deuterotrihalomethanes, C^2HX_3 (X = Cl, Br, or I), and dideuterodihalomethanes, $C^2H_2X_2$, using solid-state deuterium quadrupole spin-echo techniques (*6*). Such measurements, at least for the di- and trihalomethanes, do not suffer so severely from uncertainties due to solvent effects, arising, for example, from the use of various liquid crystals containing aromatic and other more polar groups, or to uncertainties in bond lengths, vibrational averaging, and unknown electric field gradient asymmetry parameters.

Spectra were obtained on a "home-built" spectrometer at 55.3 MHz using an 8.45 T, 3.0 in. bore Oxford Instruments (Osney Mead, Oxford, U.K.) superconducting solenoid, a Nicolet (Madison, Wisc.) 1180 computer and 1290 transient recorder, together with a variety of other digital and radiofrequency electronics. We also used a home-built solenoidal radiofrequency coil probe (sample volume ~0.8 cm^3), together with a quadrupole spin-echo sequence (*6*), for data acquisition. The 90° pulse width used was 3.3 μs. All samples (except [^{2}H]triiodomethane) were obtained from Merck, Sharpe, and Dohme (Canada), and were used without further purification. [^{2}H]Triiodomethane was prepared from [^{2}H]trichloromethane and iodoethane, as reported in the literature (*7*).

A typical experimental spectrum (displayed for the convenience of the reader as a "mirrored" on-resonance single-phase detected spectrum), together with its com-

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puter-simulated lineshape, is shown in Fig. 1, and the QCC values determined from such simulations for all species examined are given in Table 1. All asymmetry parameters were very low, in the range 0 to ±0.02.

For [^{2}H]trichloromethane, previously published deuterium QCC values vary from 149.1 to 174.7 kHz (*1, 3, 8–11*) with values measured in various liquid-crystal solvents varying from 155 to 174.7 kHz (*1, 3, 9*). Measurements from ^{2}H and ^{13}C relaxation studies and Raman lineshapes have resulted in QCC values between 153 and 158 kHz (*9, 10*) in the liquid state. The present measurement of 162.7 ± 1 kHz at 185 K agrees very well with that of 163.4 ± 0.1 kHz at 198 K made in the solid state using a double-resonance level crossing (DRLC) quadrupole resonance experiment. DRLC measurements at 77 K have given values of 166.9 ± 0.1 and 167.6 ± 0.8 kHz (*11*). For [^{2}H]tribromomethane there have only been a few QCC measurements reported, but the scatter is even larger than for [^{2}H]trichloromethane varying from 122.3 to 183.7 kHz (*2, 10–12*). There are no solid-state measurements, and the values reported in liquid-crystal solvents are unusually large, and may arise because of the use of too small an r_{CH} value. The only other reasonable QCC measurements, from ^{1}H and ^{2}H relaxation studies (*12*), also used this small r_{CH}, and again have the rather large value of 171.2 kHz. Our measurement of 166.3 ± 1 kHz is independent of such uncertainties. For [^{2}H]triiodomethane we obtain QCC = 167.5 ± 1 kHz, whereas the measurements in liquid-crystal solvents have provided values of 165.1 ± 1.4 and 173.4 ± 1.4 kHz (*2*). Thus, the solid-state NMR results for the deuterotrihalomethanes do not bear out any maximum QCC value for C^2HBr_3, but instead show only a small monotonic increase from C^2HCl_3 (162.7 ± 1 kHz) to C^2HI_3 (167.5 ± 1 kHz).

For the dideuterodihalomethanes, nematic phase results have only been reported for $C^2H_2Cl_2$ (*3, 14, 15*) and have yielded QCC = 160 kHz (*14, 15*), and more

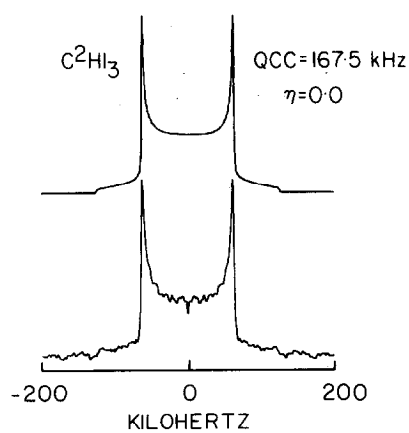

FIG. 1. Representative deuterium quadrupole-echo NMR spectrum at 55.3 MHz (corresponding to a magnetic field strength of 8.45 T) of [^{2}H]triiodomethane at 293 ± 2 K, (below) together with its computer simulation (QCC = 167.5 kHz, η = 0) (above). Spectral conditions were a 1000 s recycle time, 1 MHz data acquisition rate, 4K data points, 3.3 μs 90° pulse widths, a 40 μs τ spacing, 1000 Hz line broadening due to exponential multiplication. Data was taken using single-phase detection on resonance, and the frequency-domain spectrum is "mirrored" about zero frequency.

TABLE 1

Deuterium Quadrupole Coupling Contants for [^{2}H]Trihalomethanes and [$^2H_2$]Dihalomethanes[a]

Compound	QCC[b] (kHz)	Temperature[c] (K)
[^{2}H]Trichloromethane	162.7	185
[^{2}H]Tribromomethane	166.3	243
[^{2}H]Triiodomethane	167.5	293
[$^2H_2$]Dichloromethane	160.2	149
[$^2H_2$]Dibromomethane	160.8	190
[$^2H_2$]Diiodomethane	160.9	257

[a] All spectra were recorded using the quadrupole-echo pulse sequence at 8.45 T, as described in the text.

[b] Deuterium quadrupole coupling constant. Estimated accuracies are ±1.0 kHz. An asymmetry parameter of 0 was used in all simulations; the error here is ±0.02.

[c] Estimated accuracy is ±2 K.

recently, 167.8 ± 1.3 kHz (*3*). Results from ^{2}H relaxation studies yield QCC = 150 kHz (*15*), while NQR double-resonance studies on solid $C^2H_2Cl_2$ have resulted in QCC values of 170.93 ± 0.01 (77 K) and 159.88 ± 0.03 kHz (175.4 K) (*8, 16, 17*) and 169.6 ± 1.1 kHz (77 K) (*11*). Our measurement of 160.2 ± 1 kHz at 149 K is in reasonable agreement with the NQR values.

For the dideuterodibromo and dideuterodiiodomethanes, the only QCC data available appear to be from ^{2}H relaxation measurements in the liquid state (*18, 19*). The values for $C^2H_2Br_2$, QCC = 181 ± 1 kHz and for $C^2H_2I_2$, QCC = 175 ± 2 kHz are both considerably larger than the 160.8 ± 1 and 160.9 ± 1 kHz values obtained by us at 190 K ($C^2H_2Br_2$) and 257 K ($C^2H_2I_2$). Thus, all three directly determined dihalomethane QCC values are remarkably similar in the crystalline solid state at the temperatures indicated, consistent with our results on the deuterotrihalomethanes.

These results strongly suggest that the deuterium quadrupole coupling constants in the di- and trihalomethanes studied cover a small range in the solid-state, and that there is no maximum value for C^2HBr_3. However, even these solid-state results can of course be influenced by the presence of torsional motions, as has been noticed for $C^2H_2Cl_2$, where QCC changes from 159.88 to 170.93 kHz between 175.4 and 77 K (*17*), and also in the present study on $C^2H_2I_2$ we have observed an increase in QCC from 160.9 to 166.7 kHz from 257 to 165 K. Thus, studies over a wide range of temperatures, together with appropriate theoretical modeling of such motions, or alternatively the acquisition of data at liquid helium temperatures, and perhaps in more inert matrices such as solid Ar, should be performed to gain further insights into the electric field gradients at deuterium nuclei in such systems.

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