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Abstract

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Nuclear Quadrupole Relaxation of Deuterium in Liquids

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Bloembergen, Purcell, and Pound (^{1}) established that the interaction of the quadrupole moments of deuterium nuclei with local electric fields is the cause of the spin-lattice relaxation of deuterons in water. As far as we know, quadrupole relaxation (q.r.) of deuterons in other liquids has not been studied. Meanwhile, measurements of the q.r. time of deuterons are one of the few methods for determining the electric-field gradient at the positions of hydrogen nuclei in various chemical bonds. In (^{2}) it is emphasized that the quadrupole coupling constant (q.c.c.) of deuterium is simpler to interpret than the chemical shifts of the resonance frequency of protons in high-resolution spectra. In contrast to the abundance of published q.c.c.' s of chlorine, bromine, and some other nuclei, data on these constants for deuterium are sparse (^{2}).

In the present work, results are reported for measurements of the spin-lattice relaxation times T_1 of deuterium in 11 molecular liquids. An estimate of the magnetic dipole-dipole contribution to the measured values of T_1 showed that it may be neglected. The measured relaxation times are determined by quadrupole interactions and are described by formula (^{3}):

$$1/T_1 = {}^3/8\,(1-\eta^2/3)\,(e^2qQ/\hbar)^2\,\tau_c, \tag{1}$$

where η is the asymmetry parameter, $(2\pi)^{-1}(e^2qQ/\hbar)$ is the quadrupole coupling constant expressed in hertz, and τ_c is the correlation time of the quadrupole interaction. For the same reasons as in (^{4}), we may neglect the term depending on η. Even for $\eta = 50\%$, this neglect introduces an error of the order of 4% into the value of $(e^2qQ/\hbar)$. At the same time, the maximum value of η given in (^{2}) is 14%. Thus, for interpretation of the results the following expression was used:

$$1/T_1 = {}^3/8\,(e^2qQ/\hbar)^2\,\tau_c. \tag{2}$$

To obtain the q.c.c. from expression (2), it is necessary to know τ_c. These data, taking isotope effects into account (^{5}), can be extracted from the relaxation times of protons located at the same positions in the molecules as the deuterons under study. The correlation time can also be determined from measurements of the relaxation times of other nuclei located together with deuterium in the same groups and undergoing identical motions. If the deuterium nuclei are located in polar groups, then information on the correlation times can in some cases be obtained by studying dielectric relaxation. Times of orientational relaxation (^{6}) may also be used for this purpose.

The spin-lattice relaxation times of the deuterons were measured by the spin-echo method at a frequency of 4.4 Mc/s. To determine T_1, a sequence of 90–180–90–180° radio-frequency pulses was used. The samples were obtained from the All-Union Office "Izotop." All liquids were deoxygenated by freezing, pumping, and thawing. This cycle was repeated 3-5 times. Samples with volumes of $\sim$ 2.5 cm^3 were contained in Pyrex ampoules sealed under vacuum. The accuracy of the measurements was $\pm$10%. The temperature of the samples was maintained at $20 \pm 2°$. The results of the measurements are given in Table 1.

Table 1

Compound	Compound	Bond	T_1, sec	$\tau_c \cdot 10^{12}$, sec	(e^2qQ/h), kHz	Compound	Compound	Bond	T_1, sec	$\tau_c \cdot 10^{12}$, sec	(e^2qQ/h), kHz
Methyl alcohol	CH_3OD	O–D	0.27	18^a	119	Toluene	$C_6D_5CH_3$	C–D	0.99	3.5^c	140
Methyl alcohol	CD_3OH	C–D	4.3	–	–	*o*-Deuterotoluene	$C_6H_4DCH_3$	C–D	0.94	3.5^c	143
Ethyl alcohol	CH_3CH_2OD	O–D	0.15	34.6^b	114	*p*-Deuterotoluene	$C_6H_4DCH_3$	C–D	0.96	3.5^c	142
Ethyl alcohol	CD_3CD_2OH	C–D	0.86	–	–	Water	50% H_2O + 50% D_2O	O–D	0.46	3.5^d	206
Ethyl alcohol	CD_3CH_2OH	C–D	0.78	–	–						
Pyridine	C_5D_5N	C–D	1.03	2.8^c	153						
Benzene	C_6H_5D	C–D	1.93	1.8^c	140						

a –from dielectric-relaxation data given in (7); b –from the ratio $\tau_{C_2H_5OH}/\tau_{CH_3OH} = 1.92$ (8); c –orientational relaxation times (6); d –(1).

Here, too, the values of the reorientation times of molecules containing only protons, taken from the literature, are given. The possibility of using these times to describe the motions of deuterated molecules is justified by the fact that τ_c in most cases changes in parallel with the viscosity (6), which upon deuteration of organic compounds changes by only a few percent (9). As the reorientation times of deuterons in O–D bonds in alcohols, the values $\tau_c = \tau_D/3$ were taken, where τ_D is the dielectric-relaxation time.

The closeness of the relaxation-time values for deuterons located in the methyl and methylene groups of ethyl alcohol apparently indicates that the reorientation times of these groups are the same. The last column gives the values of the deuterium quadrupole-coupling constants obtained with the aid of equation (2). For deuterons located in C–D bonds, in different molecules the quadrupole-coupling constants do not differ greatly. Because the number of measured substances was small and exact data on the reorientation times of methyl and methylene groups were lacking, it was not possible to establish a correlation between the quadrupole-coupling constants of deuterons in C–D bonds and the NMR chemical shifts of protons in C–H bonds. One can only draw attention to the absence, beyond the limits of experimental error, of a difference between the quadrupole-coupling constants of deuterons in the ortho and para positions in the toluene molecule, and note that the chemical shifts of protons in these same positions are identical. The difference between the quadrupole-coupling constants of deuterium in the O–D bond in water and in alcohols is fairly large. One reason for this may be a not entirely correct choice of the reorientation times of the hydroxyl groups of the alcohols; another reason may be the intermolecular hydrogen bond, whose strength is not the same for alcohols and water (10). Apparently, the study of the quadrupole-coupling constants of deuterons located in O–D, N–D, and other bonds may provide additional information about the nature of the hydrogen bond.

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Note: Figure translations are in progress. See original paper for figures.