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Scalar Coupling and Spin-rotation Interactions in the ^{13}C Nuclear Magnetic Relaxation of Methyl-d_3 Bromide

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Synopsis. ^{13}C NMR relaxation times have been obtained for methyl-d_3 bromide at room temperature, from which the spin-spin coupling constant between ^{13}C and ^{79}Br has been extracted and found to be 41.6±2.0 Hz. The contribution of the spin-rotation interaction to the ^{13}C relaxation is large in this molecule. This fact may be attributed to the presence of a methyl rotor, but cannot be satisfactorily interpreted in the framework of the present theories.

The dominant relaxation mechanism of the ^{13}C nucleus in bromomethanes has been found to be scalar coupling interaction owing to the fact that the resonance frequency of ^{13}C is close to that of bromine and that bromine has its relaxation mechanism by quadrupole interaction. We have shown that the relaxation curves for bromomethanes show non-exponential decay due to the presence of two bromine isotopes with a ratio of about 1:1.[1)] By analyzing the relaxation curves we have been able to obtain the spin-spin coupling constants between ^{13}C and Br for three deuterated species, CD_2Br_2, $CDBr_3$, and CBr_4. For these species, other mechanisms contribute negligibly to ^{13}C relaxation. In methyl bromide, however, the spin-rotation mechanism may contribute to a large extent, even when the deuterated species are employed, because of the smaller size of the molecule and the presence of a methyl top. In the present paper, the spin-spin coupling constant between ^{13}C and ^{79}Br (J_{79}) for methyl-d_3 bromide has been obtained from ^{13}C relaxation time measurements, considering the contribution of the spin-rotation mechanism.

Experimental

Methyl-d_3 bromide was purchased from MSD, Canada, Ltd., and used without further purification. A high vacuum apparatus was empolyed for sampling. After several freeze-pump-thaw cycles, the sample was sealed into 8 mm dia. tube specially designed for the T_1 measurement. The sample remains in the liquid state in the sealed tube at room temperature. ^{13}C relaxation time measurements was conducted at 25.2 and 15.1 MHz with and without deuterium decoupling respectively, using a Varian XL-100-15 and a NEVA NV-14 spectrometers. Deuterium relaxation times was measured at 15.4 MHz by the XL-100-15. Other experimental details are the same as described in a previous paper.[1)]

Results and Discussion

The relaxation curves obtained for ^{13}C in methyl-d_3 bromide at 15 and 25 MHz at room temperature show non-exponential decay, as predicted. The ^{13}C relaxation curve for CD_3Br is given by:[1)]

$$\{I(\infty)-I(t)\}/I(\infty) = \exp(-t/T_1{}^{s}) + \exp(-t/T_1{}^{l}) \tag{1}$$

with $1/T_1{}^{s}=1/T_1{}^{\circ}+1/T_1{}^{79}$ and $1/T_1{}^{l}=1/T_1{}^{\circ}+1/T_1{}^{81}$ where $T_1{}^{79}$ and $T_1{}^{81}$ are the scalar relaxation (SC) times of ^{13}C bonded to a ^{79}Br and a ^{81}Br respectively, and $T_1{}^{\circ}$ is the relaxation time from other sources. The sum of the two exponentials in Eq. 1 may be separated into each exponetial by a nonlinear least squares fit to give $T_1{}^{s}$ and $T_1{}^{l}$, the result of which is shown in Table 1.

TABLE 1. RERAXATION TIMES(s) IN CD_3Br OBSERVED AT 29.8 °C

Resonance freq.	$T_1{}^{s}$	$T_1{}^{l}$	T_1 of D
15 MHz	5.85±0.33	34.0±0.4	7.97±0.18
25 MHz	6.64±0.38	36.9±0.9	

The scalar coupling constant between ^{13}C and ^{k}Br (k=79 or 81), A_k ($=2\pi J_k$), may be obtained by solving the following set of equations.

$$1/T_1{}^{k} = (2/3)A_k{}^2S(S+1)\tau_k/(1+\Delta\omega_k{}^2\tau_k{}^2) \tag{2}$$

where τ_k is the relaxation time of ^{k}Br, $\Delta\omega_k=\omega_C-\omega_{kBr}$, the resonance frequency difference, and S is the spin of bromine (3/2). $T_1{}^{\circ}$ includes the contributions from the dipole-dipole (DD) interaction between ^{13}C and D ($T_{1D}{}^{CD}$), from that between ^{13}C and Br ($T_{1D}{}^{CBr}$), from the spin rotation (SR) interaction ($T_1{}^{SR}$), and from intermolecular DD interactions ($T_1{}^{inter}$). Of these contributions $T_{1D}{}^{CD}$ may be estimated by measuring the D relaxation time to obtain the correlation time of D using the known value of the deuterium quadrupole coupling constant in this molecule (166 kHz[2)]). The contributions of $T_{1D}{}^{CBr}$ ($\approx 5\times10^3$ s) and $T_1{}^{inter}$ are so small that they can be neglected in the following calculation. Only the SR mechanism contributes to $T_1{}^{\circ}$, and, in fact, it is a large part of $1/T_1{}^{l}$, the long component of the observed decay curve. Thus, an estimation of the SR contribution is essential for obtaining an accurate value of A_k.

$T_1{}^{SR}$ and τ_k are all independent of variations in the magnetic field. Thus, the four equations such as 2 obtained from the T_1 measurements at two resonance frequencies, 15 and 25 MHz, may overdetermine the variables involved, since the independent variables are only three (A_{79}, τ_{79}, and $T_{1C}{}^{SR}$; A_{81} and τ_{81} are related to A_{79} and τ_{79} respectively). The measurements at the two fields have been carried out at 29.8 °C, and J_{79} has been determined so as to obtain agreement in τ_{79} and $T_1{}^{\circ}$ between the results at 15 and 25 MHz. The value of J_{79} thus obtained is 41.6 Hz, as shown in Table 2.

The values of J_{79} for methyl bromide and other bromomethanes[1)] are plotted against the number of bromine atoms in Fig. 1, in which a similar plot for

Table 2. Caluculated relaxation parameters

T_{1C}^{SR} (s)	τ_{79} (μs)	T_{1D}^{CD} (s)	J_{79} (Hz)	τ_{θ}^{eff}(D) (ps)	τ_{θ}^{eff}(Br) (ps)	τ_J (ps) J-diffusion		M-diffusion	
						From D	From Br	From D	From Br
40.6	0.93	803	41.6	0.307	0.82	0.059	0.058	0.184	0.30
(±1.7)	(±0.10)	(±17)	(±2.0)	(±0.008)	(±0.10)	(±0.001)	(±0.006)	(±0.004)	(±0.03)

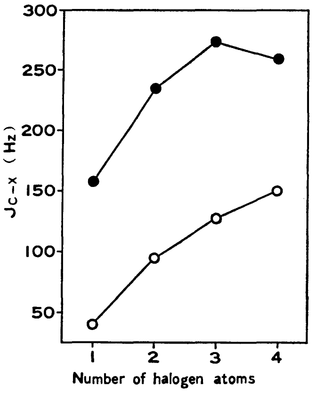

Fig. 1. Coupling Constants between ^{13}C and halogens in bromo- and fluoromethanes. ● Br, and ○ F.

fluoromethanes[3] is included for comparison. A parallelism between the two plots may be seen, *i.e.*, a monotonic increase of J_{CX} with increasing number of halogen atoms is observed. The smaller value for CF_4 than that for CHF_3 has been explained in terms of the double-bond-no-bond resonance effect.[4] In bromomethanes, such an effect seems to contribute little due to the less ionic character of Br.

McClung has developed the extended diffusion theory for molecular reorientation, in which rotational diffusion occurs through larger angle in liquid.[5] Assuming the J- or M-diffusion models, the angular momentum correlation time of the molecular reorientation, τ_{θ}^{eff}, which in turn, for methyl-d_3 bromide, is obtained independently from the D or Br relaxation time. Thus, the τ_J calculated from the D relaxation time should agree with that obtained from the Br relaxation time at the same temperature. As seen from Table 2, the two values well agree with each other in the J-diffusion model, but do not so in the M-diffusion model. This is consistent with the fact that the J-diffusion model also applies to CD_3CN,[6] which has nearly the same moment of inertia and approximately the same molecular geometry as CD_3Br.

The SR relaxation time in CD_3Br is *ca.* 40 s at room temperature. This value appears to be rather short, but may be compared with the values reported for CH_3CN (*ca.* 33 s at 30 °C[7]) and CH_3I (*ca.* 23.5 s at 25 °C[8]), molecules of similar size and structure, which may be roughly converted to the values for deuterated species by multiplying 1.39,[7] and then 46 and 33 s respectively. According to McClung,[5] the SR relaxation time may be calculated for τ_J and the known values of the SR coupling constants. The latter can be estimated from the relation which connects them to the average shielding value and the chemical shift anisotropy, $\Delta\sigma$.[9] Using the chemical shift data and $\Delta\sigma = -10$ ppm,[10] and taking the coupling constant of methane (-15.94 kHz[11]) as a reference, the SR coupling constant for CD_3Br is found to be $C_{\perp} = -0.96$ and $C_{//} = -9.86$ kHz.

The T_{1C}^{SR} calculated in this way is, however, too long to explain the experimental data, *i.e.*, 271 s at 29.8 °C, or 8 times the experimental value. This discrepancy between the experimental and estimated values is large, and a similar trend has been observed in other similar compounds. For CH_3I, the value estimated in a similar manner is 25 times the experimental value.[8] Goldammer *et al.*[7] assumed the SR coupling constants for methyl carbon which are much larger than that estimated by the chemical shift data in order to fit the experimental values of T_{1C}^{SR}. The calculations in these previous works are more or less based on the rotational diffusion theory of Hubbard[12] and Huntress,[13] which differs from that of McClung and is somewhat classical. However, the large discrepancy between the observed and the estimated values does not appear to stem from the calssical nature of the theory involved. All of the results including that of the present work suggest that the discrepancy arises from the presence of a methyl rotor, *i.e.*, the presence of a "fast internal rotation," as indicated by Gillen *et al.*[8] McClung's theory, which permits diffusive steps of arbitrary sizes, has been well adopted for reigid molecules such as benzene.[9] For the molecules with a methyl rotor, however, it appears to be still incomplete for the full description of the molecular reorientation. A more improved theory including the fast internal rotation is clearly needed.

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