Ratio of the quadrupole coupling of bromine isotopes in a CH_3Br molecule

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We determined from the quadrupole spectrum of the CH_3Br molecule the ratio of the quadrupole couplings for Br^{79} and Br^{81} nuclei, which, because of its difference from the corresponding ratio in atomic bromine, indicates that a pseudoquadrupole effect or nuclear polarization occurs in this molecule.

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1. The search for a pseudoquadrupole effect (PQE) and nuclear polarization (NP) in molecules by the method of radiospectroscopy of molecular beams did not give positive results,[1,2] although the first attempts to detect these effects were made long ago.[3]

As the calculation shows, the energy of the PQE and NP comprises only a small fraction of the total energy of the quadrupole interaction of a nucleus with the electric field of the molecule. A well-known method of detecting the PQE and NP involves the study of the dependence of the quadrupole coupling of a given nucleus on the molecular environment: the ratio of the quadrupole couplings of two isotopes of the same element, which are "located" in different molecules, is usually determined.

2. Using a double-resonance pulse spectrometer,[4] we investigated the quadrupole spectrum of the CH_3Br molecule. The magnetic structure of the spectrum was resolved at the line width of about 2 kHz and a measurement accuracy of the frequency of ± 0.2 kHz.

For the calculation of the constants the energy of the quadrupole and of the $\mathbf{I}\cdot\mathbf{J}$

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interactions was determined by the relation (1):

$$E(J, K, F_1) = \left(\frac{3K^2}{J(J+1)} - 1\right) f(I, J, F_1) eqQ(J, K) + f^{(2)} \frac{(eqQ_0)^2}{B_0} + f^{(3)} \frac{(eqQ_0)^3}{B_0^2} \tag{1a}$$

$$+ \frac{1}{2}\left[C_N + (C_K - C_N)\frac{K^2}{J(J+1)}\right]\left[F_1(F_1+1) - I(I+1) - J(J+1)\right] \ldots \tag{1b}$$

In line (1a), which is the quadrupole part of the interaction energy, $eqQ(J, K)$ is the quadrupole coupling, which in the nonrigid molecule depends on the rotational state, $f(I, J, F_1)$ is the Casimir function, and $f^{(2)}$ and $f^{(3)}$ are the second- and third-order corrections; the term (1b) is the energy of the **I·J** interaction.

TABLE I.

	CH_3Br^{79}		CH_3Br^{81}
		B_0 MHz	
	9568.19		9531.83
		eqQ_0 kHz	
	577135.2		482132.1
J, K		$eqQ(J, K)$ kHz	
2,2	577107.94(80)		482111.16(80)
3,3	577089.40(64)		482094.19(64)
4,4	577064.06(57)		482073.49(57)
		$C_N + (C_K - C_N)\frac{K^2}{J(J+1)}$ kHz	
2,2	16.47(8)		17.60(8)
3,3	16.86(6)		18.12(6)
4,4	17.22(5)		18.52(5)

TABLE II.

J,K	2.2	3.3	4.4
$R_M = \frac{eqQ(\mathrm{Br}^{79})}{eqQ(\mathrm{Br}^{81})}$	1.1970433(37)	1.1970470(30)	1.1970458(26)

The results of the measurements are given in Table I, which contains values of the quadrupole couplings and of the magnetic **I·J** interactions for the rotational states of the CH_3Br molecule with $J = K = 2$, 3, and 4. It also gives the quadrupole coupling of the zeroth approximation and rotational constants used in calculating the second- and third-order corrections in Eq. (1).

The ratios of the quadrupole couplings of Br^{79} and Br^{81} nuclei in the CH_3Br molecule are given in Table II. These ratios should be compared with an analogous ratio for the atomic bromine in Ref. 5 $R_A = 1.1970568$ (15).

The difference between R_M and R_A, which exceeds the experimental error given in the parentheses in units of the last decimal place, indicates that at least one of the effects, PQE or NP, exists. A specific contribution to the difference $R_M - R_A$ can also be made by the change of the quadrupole coupling magnitude because of the difference in the energy of the zero-point vibrations of the Br^{79} and Br^{81} nuclei. A preliminary estimate shows, however, that in this case the isotopic correction for zero-point vibrations is within the limit of experimental error.

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