Quadrupole Spectrum of $BiCl_3$†

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Pure nuclear quadrupole resonance absorptions were observed for Bi^{209}, Cl^{35}, and Cl^{37} nuclei in polycrystalline $BiCl_3$ at both room and liquid air temperatures. Line assignments and the evaluation of the electric field gradient asymmetry parameter η allow the following coupling constants to be calculated: $|eQq|_{Bi}=318.76$ Mc/sec for $\eta=0.555$; $|eQq|_{Cl^{35}}=30.196$ Mc/sec, 38.310 Mc/sec. Two "forbidden" $|\Delta m'|=2$ transitions were observed. A brief discussion of the data in connection with chemical bonding in the solid is given.

INTRODUCTION

As a continuation in the study of the nuclear quadrupole resonance[1] of Bi^{209}, solid $BiCl_3$ was investigated. Both Cl and Bi resonances were observed in the quadrupole spectrum of this molecule. Even though the couplings of both constituents of the molecule are known, a description of the chemical bonding is made difficult because the solid state structure is evidently unknown. Therefore, the data presented may perhaps become more meaningful when the crystal structure is determined.

EXPERIMENTAL

A 30-cc polycrystalline sample of $BiCl_3$ was dried in vacuum and sealed in a glass tube at atmospheric pressure. Due to the deliquescent nature of $BiCl_3$, a dry sealed sample is necessary to maintain a high Q in the oscillator tank circuit.

The resonance absorption lines were observed by means of super-regenerative detection. At room temperature, all but the Cl^{37} lines were observable by frequency modulating the oscillator and oscilloscopic display. The temperature was maintained relatively constant by water-cooling the copper radio-frequency shield surrounding the sample. During runs at liquid air temperature a forty-cycle off-on square-wave Zeeman-modulation magnetic field together with conventional narrow-band phase-sensitive detection techniques were used.

The majority of the resonances observed were so broad that side-bands due to super-regenerative detection were not resolved when using the spectrometer with a normal high-Q tank circuit. In order to be able to use sufficiently high quench frequencies for side-band resolution, the Q of the tank circuit was lowered to approximately one-half its original value by shunting the tank with an appropriate resistor. With this modification, observations of the relative motion of the line, side-bands, and marker lattice over a relatively wide range of quench frequencies were possible. Hence, one is able to eliminate errors due to guessing the center of an unresolved line-side-band combination.

It was possible to apply 10-mw peak power to the sample without causing noticeable saturation broadening.

ASSIGNMENTS

Assignments for the Cl resonances were made by using the known[2] ratio of the quadrupole moments for the Cl^{35} and Cl^{37} isotopes. A $Cl^{35,37}$ spin of 3/2 allows only one line per lattice site per isotope. The set of four lines observed may thus be interpreted as indicating two nonequivalent lattice sites in the unit cell. Since no value of the asymmetry parameter η was determined for the field gradient of the Cl nucleus, the coupling constant $|eQq|$ was calculated by doubling the observed frequency, i.e., assuming $\eta=0$.

The identification of the four $|\Delta m|=1$ transitions and the calculation of the asymmetry parameter for the Bi^{209} nucleus follows a method proposed by Cohen.[3] One plots calculated frequency ratios as a function of η. Because a given value of η implies a unique set of frequency ratios, the measured frequency ratios should intersect the calculated ratios in a verticle line over the η appropriate for a fit of the data. In addition to the evaluation of η, the identifications of the transitions are

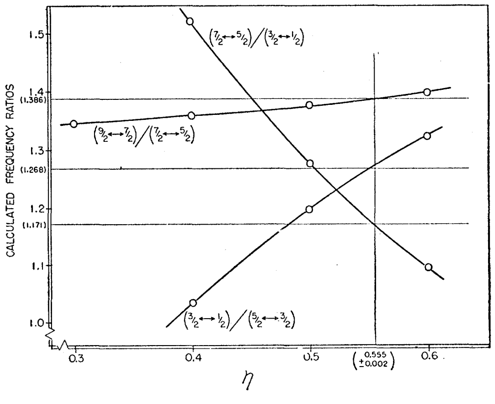

Fig. 1. Determination of η and line assignments.

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† This research was supported by The United States Air Force through the Office of Scientific Research of the Air Research and Development Command.

[1] Robinson, Dehmelt, and Gordy, Phys. Rev. **89**, 1305 (1953).

[2] R. Livinston, Phys. Rev. **82**, 289 (1951).

[3] M. H. Cohen, Phys. Rev. **96**, 1278 (1954).

TABLE I. Allowed transitions in $BiCl_3$: measured frequencies all accurate to at least ±11 kc/sec at 299°K, ±20 kc/sec at 83°K.

Lattice site	Temp. (°K)	Observed frequency (Mc/sec)	Observed frequency ratios	Calculated relative frequency factors r_i	Calculated frequency ratios	Assignments	$\|eQq\|$ (Mc/sec)
		15.955				Cl^{35}	
I			1.2688				38.310
		12.573				Cl^{37}	
		19.155				Cl^{35}	
II			1.2690				30.196
		15.0976				Cl^{37}	
	299±1°				$\eta=0.555$ ±0.002	Bi^{209}	$24\nu_i/r_i$
		51.740		3.898		$(9/2\leftrightarrow7/2)$	318.56
			1.386		1.387		
		37.340		2.810		$(7/2\leftrightarrow5/2)$	318.92
			1.171		1.1708		
		31.876		2.400		$(3/2\leftrightarrow1/2)$	318.76
			1.268		1.2685		
		25.131		1.892		$(5/2\leftrightarrow3/2)$	318.79
							Average 318.76±0.20
		15.849					
I			1.268				
		12.498					
		19.531					
II			1.269				
		15.387					
	83°				$\eta=0.583$ ±0.008	Bi^{209}	$24\nu_i/r_i$
		52.704		3.889		$(9/2\leftrightarrow7/2)$	325.25
			1.391		1.393		
		37.900		2.792		$(7/2\leftrightarrow5/2)$	325.79
			1.124		1.123		
		33.726		2.486		$(3/2\leftrightarrow1/2)$	325.59
			1.302		1.301		
		25.905		1.911		$(5/2\leftrightarrow3/2)$	325.34
							Average 325.5±0.3

determined. Figure 1 shows this solution on an expanded scale; in this case, the value of η is determined to an accuracy limited by the graphical solution.

The magnitude of the coupling constant $|eQq|$ can now be found by plotting the relative frequency factors against η. This factor, r_i, is defined by the equation

$$\nu_i = r_i |eQq| / 24,$$

where ν_i is the frequency of the ith transition. Using the calculated value of η, one can now determine the relative frequency factor for each transition. See Fig. 2. By using the observed frequencies and the calculated r_i, $|eQq|$ is given by the above formula. Results are listed in Table I.

The energy levels used in determining the calculated frequency ratios in Fig. 1 and the relative frequency factors in Fig. 2, were calculated by Cohen[3] by numerical solution of the fifth-order secular equation appropriate to the 9/2 spin of the Bi^{209} nucleus. Bersohn's fourth-order formulas[4] obtained by perturbation methods cannot be used for so large a value of the asymmetry parameter, 0.555. In fact, with a 9/2 spin and asymmetry greater than 0.1, the perturbation formulas produce a significant error in the value of the $(3/2\leftrightarrow1/2)$ transition for $|eQq| \geq 300$ Mc/sec. In contrast to this the $(9/2\leftrightarrow7/2)$ transition is relatively insensitive to the asymmetry parameter and the value

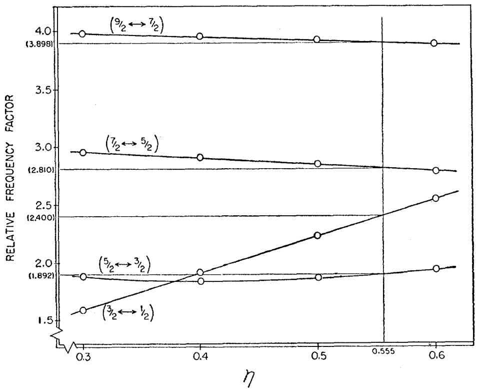

FIG. 2. Determination of the relative frequency factors, r_i.

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[4] R. Bersohn, J. Chem. Phys. **20**, 1505 (1952).

of $|eQq|$ calculated from the perturbation formula,

$$|eQq| = 6\nu(9/2 \leftrightarrow 7/2)/(1-0.08095\eta^2 - 0.0043\eta^4),$$

agrees with that determined graphically.

FORBIDDEN TRANSITIONS

Heretofore, only allowed magnetic dipole transitions $|\Delta m| = 1$ have been reported for pure nuclear quadrupole resonance.[5] In the case of BiCl$_3$, as a result of the large asymmetry in the field gradient, the magnetic sub-states for which $|\Delta m'| = 2$ are connected providing an observable transition probability. The $(1/2 \leftrightarrow 5/2)$ and $(3/2 \leftrightarrow 7/2)$ transitions were observed to within the experimental error at frequencies corresponding to the sum of the two appropriate $|\Delta m| = 1$ transitions; i.e., the sum of $(1/2 \leftrightarrow 3/2)$ and $(3/2 \leftrightarrow 5/2) = (1/2 \leftrightarrow 5/2)$. See Table II. Although no careful measurement of the relative intensities of the allowed and forbidden transitions was attempted, the order-of-magnitude agreement with Cohen's calculations was experimentally confirmed. See Fig. 3 for a recording of the $(1/2 \leftrightarrow 5/2)$ transition.

The possibility of d-admixture in the orbitals of the Bi^{209} together with the 9/2 spin of this nucleus allow a magnetic octuple interaction. One effect of such interaction should be the mixing of the $|m| = 3/2$ levels, thereby removing the $\pm m$ degeneracy. However, the energy difference involved here should be several orders of magnitude smaller than that of the electric quadrupole interaction so that no observable effect should be noticed with the resolution attainable in this type of experiment. A recording of the $(3/2 \leftrightarrow 5/2)$ line with the spectrometer operating in the regenerative mode revealed no broadening attributable to the above effect.

DISCUSSION

The structure of BiCl$_3$ in the solid state was not found in the literature. Nevertheless, from the observed Cl resonances two nonequivalent positions in the unit cell may be inferred for this nucleus. In addition, the line widths and intensities indicate approximately equal numbers, 1:1 or 1:2, of Cl nuclei in each of these positions at both room and liquid air temperatures. Variation in spectrometer sonativity and possible distortion of the line shape due to super-regenerative detection prevents one from making more definite conclusions.

TABLE II. "Forbidden" transitions in BiCl$_3$.

Observed frequency (Mc/sec)	Assignments	Sum of $\|\Delta m\| = 1$ transitions (Mc/sec)
56.98	$(5/2 \leftrightarrow 1/2)$	$(5/2 \leftrightarrow 3/2) + (3/2 \leftrightarrow 1/2)$ 57.01
62.49	$(7/2 \leftrightarrow 3/2)$	$(7/2 \leftrightarrow 5/2) + (5/2 \leftrightarrow 3/2)$ 62.47

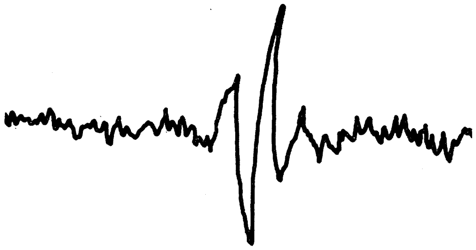

FIG. 3. The $(1/2 \leftrightarrow 5/2)$ pure quadrupole transition (forbidden transition) of Bi^{209} in BiCl$_3$.

The low value of the Cl coupling indicates an ionic character of the order of 65% for the BiCl bonds. The effect of asymmetry in the field gradient at the Cl nucleus may be seen from the formula for 3/2 spin[6]:

$$|eQq| = 2\nu(3/2 \leftrightarrow 1/2)/(1+\tfrac{1}{3}\eta^2)^{\frac{1}{2}}.$$

Thus, if $\eta = 0$, the coupling is lower, and larger amounts of hybridization and/or ionic character are necessary than indicated above. However, for an asymmetry of 0.6 the coupling is reduced only by 5 percent from that for zero asymmetry so that effects of the asymmetry on the coupling may be neglected in this approximate treatment.

In discussing crystal structure in connection with the coupling, it must be remembered that the principle contributor to the field gradient will be p-electrons—the direct contribution of d-electrons will be negligible. However, d-electrons will play a significant role in determining the crystal structure. This also applies to p-d hybridized orbitals which contain at least one electron. Therefore, for heavy atoms in which d-hybridization is likely, s-p hybridization alone may not be sufficient to describe the resulting bond angles and coupling. In cases where s-p hybridization alone is thought to be sufficient, one can relate the percent s-character, α, to the bond angle B-A-B, γ, in AB_3 molecules by the formula

$$\alpha = -\cos\gamma/(1-\cos\gamma),\ 0 \leq \gamma \leq \tfrac{1}{3}.$$

This formula was derived by the assumption that bonds are formed according to the principle of maximum overlap. Thus one can calculate[7] the molecular coupling $(eQq_{zz})_A$ as a function of the bond angle, the percent ionic character β of each bond, and $(eQq_0)_A$ which is the coupling due to a single p-electron in the magnetic substate $m_l = 0$:

$$(eQq_{zz})_A = \frac{-3\cos\gamma}{(1-\cos\gamma)}(1+2\beta)(eQq_0)_A.$$

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[5] G. Lamarche and G. M. Volkoff, Can. J. Phys. **31**, 1010 (1953), suggested the possibility of observing forbidden transitions in LiAl(SiO$_3$)$_2$. R. M. Cotts and W. D. Knight, Phys. Rev. **96**, 1285 (1954), attempted without success to observe such transitions in KNbO$_3$.

[6] R. V. Pound, Phys. Rev. **79**, 685 (1950).

[7] Compare Gordy, Smith, and Trambarulo, *Microwave Spectroscopy* (John Wiley and Sons, Inc., New York, 1953), p. 281.

This assumes a positive charge on A resulting from the ionic character of the bond. An alternate expression[8] using the coupling $(eQq')_A$ along the bond direction due to one electron in the hybridized bonding orbital is

$$(eQq_{zz})_A=-3\cos\gamma(1+2\beta)(eQq')_A.$$

Making the simplifying assumption that the AB_3 structure applies for crystalline $\mathrm{BiCl_3}$, 3% s-character in the Bi bonding orbital or a Cl-Bi-Cl angle of 91.2° is given by the formulas for α and $(eQq_{zz})_A$. A value[1] of 1500 Mc/sec was used for $(eQq_0)_{\mathrm{Bi}}$ in this calculation. An s-character of zero would indicate pure orbitals of Bi, i.e., a Cl-Bi-Cl angle of 90°, and the coupling due to p-electrons would vanish.

If one assumes that individual $\mathrm{BiCl_3}$ molecules exist in the solid, Gordy's formulas[9] may be applied. These are:

$$\beta_\sigma=1-\rho_q-\gamma_\pi/2=|x_{\mathrm{Cl}}-x_{\mathrm{Bi}}|/2,$$

$$x=0.31\left[\frac{n+1+c}{r}\right]+0.5,$$

where $\rho_q\equiv|\text{molecular } eQq/2\times\text{atomic } eQq|$ for halogen, $\beta_\sigma=$ ionic character of the σ component of the bond, $\gamma_\pi=\pi$ character of the bond, $x=$ electronegativity, $n=$ number of electrons in the unfilled shell of the neutral atom, $c=$ positive charge in electron units on the atom, $=3(\beta_\sigma-\gamma_\pi)$ for AB_3 molecule, and $r=$ covalent radius. Solving the above equations simultaneously, with $x_{\mathrm{Cl}}=3.0$, $\rho_q=35.1/109.74=0.32$, $n=5$, $r=1.46$, we have $\beta_\sigma=0.53$ and $\gamma_\pi=0.29$.

Gordy has demonstrated the applicability of the above formulas to several molecules in the solid state where each molecule essentially retains its identity. That so large a value of π character is indicated by the formulas may be taken as evidence that a significant amount of cross-bonding occurs in the solid $\mathrm{BiCl_3}$. Only 9% π character is found for $\mathrm{SnCl_4}$ and only 14% for $\mathrm{GeCl_4}$. If one assumes 14% normal π bonding in the BiCl bonds, there would be roughly 15% cross bonding. Such cross bonding should be expected for polar molecules in the solid state. The tetrahedral structure observed for gaseous[10] $\mathrm{BiCl_3}$ would require an asymmetry parameter of zero; the large value of η observed is an indication of distortion from the C_{3v} symmetry and again points to cross bonding. The cross bonding would probably involve p-d hybridized orbitals as in $\mathrm{I_2}$.

The effects of change in temperature may also indicate cross-bonding. That η decreases with increasing temperature is consistent with the view that intermolecular bonds are weakened with rising temperature. However, one might expect that such loosening of the intermolecular bonds would cause the field gradient q_{zz} to increase with temperature. This effect is in opposition to the averaging of q_{zz} due to the thermal motion of the crystal lattice which results in a negative temperature coefficient for q_{zz}. If one corrects for the change in frequency at liquid air temperature due to the change in η, there remains a difference in frequency compared with room temperature which implies for $(q_{zz})_{\mathrm{Bi}}$ a net negative temperature coefficient whose magnitude agrees with that expected for such an averaging process[11]; i.e., a temperature coefficient of $\approx -10^{-4}/°\mathrm{C}$.

A structure of the $\mathrm{BiI_3}$ type, in which the Bi is surrounded octahedrally by six I, can be rejected for $\mathrm{BiCl_3}$ on the basis that a perfect octahedral surrounding the Bi would produce a zero field gradient. Even if the octahedra were distorted, if C_{3v} symmetry remained, there would result zero symmetry.

A dimeric molecular structure, $\mathrm{Bi_2Cl_6}$, similar to that of $\mathrm{Al_2Cl_6}$ is evidently not possible because an unshared pair of electrons occupies an orbital in the plane containing the bonds which would be supposed to resonate.

ACKNOWLEDGMENTS

Grateful acknowledgment is given for discussions with Professor Walter Gordy and Dr. Masataka Mizushima.

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[8] This expression, with a change in sign, has been given by S. Kojima *et al.*, J. Phys. Soc. Japan **9**, 805 (1954).

[9] Walter Gordy, Discussions Faraday Soc. (to be published).

[10] H. A. Skinner and L. E. Sutton, Trans. Faraday Soc. **36**, 681 (1940).

[11] H. G. Dehmelt and H. Kruger, Z. Physik **129**, 401 (1951).