

Pure Quadrupole Spectrum of Cyanuric Chloride

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Citation: *The Journal of Chemical Physics* **27**, 602 (1957); doi: 10.1063/1.1743791

View online: <http://dx.doi.org/10.1063/1.1743791>

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TABLE I.

$T^{\circ}\text{K}$	D_{Na}	D_{NO_3}	$(D_{\text{Na}}+D_{\text{NO}_3})$	$(D_{\text{Na}^+}+D_{\text{NO}_3^-})$	D_{Na^+}	$D_{\text{NO}_3^-}$	D_{NaNO_3}	D'_{Na^+}	$D'_{\text{NO}_3^-}$	t_{Na^+}	$t_{\text{NO}_3^-}$
581	1.75	1.08	2.83	2.27	1.47	0.80	0.28	1.49	0.82	0.65	0.35
601	2.00	1.26	3.26	2.56	1.65	0.91	0.35	1.69	0.93	0.64	0.36
621	2.29	1.44	3.73	2.86	1.85	1.00	0.44	1.91	1.05	0.65	0.35
641	2.58	1.64	4.22	3.18	2.06	1.12	0.52	2.10	1.17	0.65	0.35

(1.12×10^9) , $D_{\text{Na}^+} + D_{\text{NaNO}_3} = D_{\text{Na}}$ and $D_{\text{NO}_3^-} + D_{\text{NaNO}_3} = D_{\text{NO}_3}$. The calculated values are listed in Table I, from which the heats of activation for diffusion are found to be 4290, 4040, and 7610 cal/mole for Na^+ , NO_3^- , and Na^+NO_3^- , respectively.

Alternatively, D_{Na^+} and $D_{\text{NO}_3^-}$ are calculated from η_{NaNO_3} ⁵ through the Stokes-Einstein relationship by taking $r_{\text{Na}^+} = 0.98 \text{ \AA}$ and $r_{\text{NO}_3^-}$ of the triangular NO_3 radical as 1.78 \AA which is the sum of the N—O bond length (1.21 \AA) and the double bond radius of O (0.57 \AA). The values obtained are listed as D'_{Na^+} and $D'_{\text{NO}_3^-}$ in Table I. It can be seen that the agreement between D_{Na^+} and D'_{Na^+} and that between $D_{\text{NO}_3^-}$ and $D'_{\text{NO}_3^-}$ are very good. This seems to indicate that, as in the case of NaCl, the Stokes-Einstein equation is valid and the ion pair plays a part in the diffusion process.

The transport numbers of Na^+ and NO_3^- , calculated from D_{Na^+} and $D_{\text{NO}_3^-}$, are listed as t_{Na^+} and $t_{\text{NO}_3^-}$ in Table I. Comparison of these calculated values with those obtained experimentally would be of great interest. Unfortunately the latter are not available at the present time.

† Financial support by the U. S. Atomic Energy Commission during the preparation of this note is acknowledged.

¹ Borucka, Bockris, and Kitchener, *J. Chem. Phys.* **24**, 1282 (1956).

² Van Artsdalen, Brown, Dworkin, and Miller, *J. Am. Chem. Soc.* **78**, 1772 (1956).

³ *International Critical Tables*, Vol. 6, p. 149.

⁴ *International Critical Tables*, Vol. 3, p. 24.

⁵ *Handbook of Chemistry* (Handbook Publishers, Inc., Sandusky, 1952), 8th Edition, p. 1701.

Pure Quadrupole Spectrum of Cyanuric Chloride

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(Received April 15, 1957)

IN the previous paper¹ we reported the pure quadrupole spectra due to Cl^{35} of phosphonitrile chlorides, one of which was the trimer $(\text{PNCl}_2)_3$ which had a benzene-like heterocyclic ring. Now we are going to report the spectrum of another heterocyclic compound, cyanuric chloride $(\text{CNCl})_3$, where the C—Cl bonds

seem to be directed in the same plane with the ring, and the double bond character as well as the ionic character may play important roles on resonance frequencies.

This compound² was prepared from cyanuric acid by chlorination with phosphorus pentachloride at 190°–195°C in phosphorus oxychloride as the solvent, and was purified by recrystallization from the chloroform solution and then by sublimation in a long test tube. The sample thus obtained was found to melt at 146°C, which was in good agreement with the value already known.³

The pure quadrupole spectrum of the compound was observed by means of the usual frequency modulated superregenerative spectrometer.¹ The resonance frequencies due to Cl^{35} were found to be 36.323 and 36.338 Mc/sec at 285°K, and the lines were so closely spaced that they were observed without interference of the side bands. The spectrum is shown in Fig. 1,

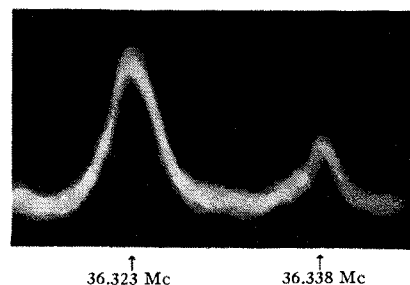


FIG. 1. Photograph of Cl^{35} resonance lines of cyanuric chloride at 285°K.

from which chlorine atoms corresponding to the lower frequency are supposed to be more abundant than the others,⁴ presumably the ratio being 2:1. However, further detailed information about the crystal structure of this compound has not been found.

On the other hand, it will be noticed that the resonance frequencies of cyanuric chloride are slightly higher than those of 1,3,5-trichlorobenzene which were found recently to be 35.036, 35.320, and 35.564 Mc/sec at 295°K by Bray *et al.*⁵ This result is evidently contrary to that of 2-chloropyridine, where the resonance frequency is lower than that of chlorobenzene.⁶ Therefore, three nitrogen atoms symmetrically replaced in a benzene ring seem to decrease the ionic character of C—Cl bond, compensating the increased double bond character. More quantitative considerations about the

effects of nitrogen atoms in the heterocyclic rings will be seen elsewhere.

¹ H. Negita and S. Satou, *J. Chem. Phys.* **24**, 621 (1956); *Bull. Chem. Soc. Japan* **29**, 426 (1956).

² *Beilsteins Handbuch der Organischen Chemie* (Julius Springer, Berlin, 1937), 4 Aufl., Vol. XXVI, p. 35.

³ C. D. Hodgman, *Handbook of Chemistry and Physics* (The Chemical Rubber Company, Cleveland, 1954), 36th edition, p. 1128.

⁴ R. Livingston, *J. Phys. Chem.* **57**, 496 (1953).

⁵ Bray, Barnes, and Bersohn, *J. Chem. Phys.* **25**, 813 (1956).

⁶ Segel, Barnes, and Bray, *J. Chem. Phys.* **25**, 1286 (1956).

Line Width of the Pure Quadrupole Resonance of Bromine in KBrO_3 [†]

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SINCE the two equally abundant bromine isotopes have the same spin number $\frac{3}{2}$ and the isotope with the larger magnetic moment has the smaller quadrupole moment, comparison of the line widths of the two isotopes in one and the same chemical compound should give information about the origin of the line width. From this point of view, measurements were made previously on NaBrO_3 ^{1,2} which was known to give the sharpest resonance of all the bromine compounds, and it was concluded that the full width at half-maximum intensity of about 4 kc/sec is due to the magnetic dipolar interaction. However, since Abragam and Kambe's theory of dipolar broadening³ (hereinafter referred to as AK) is not applicable to NaBrO_3 because of four different directions of the electric field gradient in this substance, comparison of the theory with the experiment is not possible.

KBrO_3 is of interest in this respect, because the dipolar contribution to the second moment of the resonance line can be calculated exactly using AK.

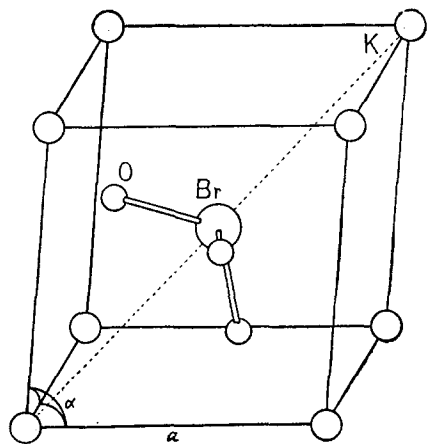


FIG. 1. Crystal structure of KBrO_3 . $a = 4.403 \text{ \AA}$, $\alpha = 86^\circ 0'$.

Therefore, as a continuation of the previous work on NaBrO_3 , measurements of the second moments were made on KBrO_3 at 0°C . The crystal structure is rhombohedral⁴ and is shown in Fig. 1. The direction of the electric field gradient is that of the body diagonal which is the threefold axis of symmetry. Since the oxygen nucleus has no magnetic moment, interactions between bromine nuclei themselves and between the bromine and the potassium nuclei contribute to the second moment. The result of calculation of the second moment is given in Table I.

The resonance frequency of Br^{79} is 173.7 Mc/sec at 0°C , and that of Br^{81} , 145.1 Mc/sec.^{5,6} The experimental apparatus and procedure are described in reference 2. However, in order to get better precision, two recorders were used; the derivative curve and the 6 kc/sec beat were recorded simultaneously as shown in Fig. 2. The correction for the finite amplitude of frequency modulation was made using Andrew's formula,⁷ the amplitude being 0.7–1.2 kc/sec. The samples used were assemblages of small crystal plates prepared by means of very slow recrystallization from aqueous solutions of pure KBrO_3 which was purified by repeated recrystallizations. Large single crystals are not obtainable by this means. Measurements were made on several samples, but only the results on the sample which gives the sharpest resonance are given below.

$$\langle \Delta\nu^2 \rangle_{79} = 4.75 \pm 0.16 \text{ (kc/sec)}^2,$$

$$\langle \Delta\nu^2 \rangle_{81} = 3.56 \pm 0.15 \text{ (kc/sec)}^2.$$

This sample gives sharper resonance than NaBrO_3 , and therefore seems to give the sharpest resonance of all the bromine compounds.

Unlike the case of NaBrO_3 , the line of Br^{79} is broader than that of Br^{81} , despite the fact that the magnetic moment is less than that of Br^{81} . Furthermore, the second moments are much greater than those calculated using AK. The line width is due to the dipolar interaction in NaBrO_3 . This can be expected to be the case in KBrO_3 , provided that the crystals are perfect. It is probable therefore that the crystal strain is primarily responsible for the observed width. Since second moments are additive, subtraction of the dipolar contribution from the observed second moment will give the contribution of the strain. The ratio of the contributions of the strain for the two isotopes should be equal

TABLE I. Dipolar contribution to the second moment of the resonance line, in units $(\text{kc/sec})^2$.

Isotope	$R-R^a$	$R-N^b$	$R-K^c$	Total
Br^{79}	0.182	0.164	0.025	0.371
Br^{81}	0.245	0.164	0.029	0.438

^a $R-R$ signifies the contribution of the interaction between the resonant bromine nuclei themselves, as calculated using formula (10) of AK.

^b $R-N$ signifies the contribution to the line width of the resonant nuclei from the nonresonant bromine nuclei, as calculated using formula (12) for the case B_2 .

^c $R-K$ signifies the contribution to the line width of the resonant nuclei from the potassium nuclei, as calculated using formula (12) for the case B_2 .