Pure Quadrupole Resonance of Nitrogen-14 in Potassium Thiocyanate and Potassium Selenocyanate

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(Received January 14, 1967)

Although a number of nitrogen-containing compounds have been studied by use of the pure quadrupole resonance technique, no reports have ever been published on the pure quadrupole resonance of nitrogen in ionic crystals. Heretofore, the quadrupole coupling constant of nitrogen in ionic crystals has been determined from the quadrupole splitting in nuclear magnetic resonance spectra of ammonium dihydrogen phosphate,1) potassium azide,2) sodium nitrate,3) *etc.* This paper demonstrates the applicability of pure quadrupole resonance to the study of nitrogen quadrupole interactions in ionic crystals.

The resonance lines were observed by means of a modified Pound-Watkins type spectrometer already described.4) Resonance frequencies were determined by frequency modulation using a TR-5178 universal counter from Takeda Riken Company and the genuineness of the lines was checked by Zeeman modulation. Commercial preparations of potassium thiocyanate and potassium selenocyante were purified by recrystallization. Each sample (*ca.* 20 m*l*) was melted in a glass tube in order to increase the filling factor.

Both potassium thiocyanate and potassium selenocyanate showed a pair of closely spaced resonance lines attributable to ν^{I} and ν^{II}, indicating that the asymmetry parameter is finite. Table 1 shows the quadrupole coupling constant and the asymmetry parameter evaluated from the observed frequencies.

TABLE 1. QUADRUPOLE COUPLING CONSTANT AND ASYMMETRY PARAMETER OF ^{14}N AT LIQUID NITROGEN TEMPERATURE, 78—79°K

Compound	KSCN	KSeCN
ν^{I}, kc/sec (S/N)	1840.6 ± 0.1 (6)	2169.0 ± 0.1 (5)
ν^{II}, kc/sec (S/N)	1806.5 ± 0.1 (6)	2098.4 ± 0.1 (8)
eQq, kc/sec	2431.4 ± 0.2	2844.9 ± 0.2
η, %	2.81 ± 0.02	4.97 ± 0.02

The quadrupole coupling constant of potassium thiocyanate is much smaller than those of organic thiocyanates (3515.4—3590.3 kc/sec) already studied,4) presumably because a thiocyanate group bears a negative charge in potassium thiocyanate crystals whereas it forms a covalent bond with a carbon atom in organic thiocyanates.

Both compounds show a finite asymmetry parameter. X-ray crystal analysis5) has shown that linear thiocyanate anions exist in potassium thiocyanate crystals. Accordingly, the field gradient due to charges within the anion is expected to be axially symmetric at the nitrogen nucleus. The small asymmetry parameter is attributable to the asymmetry of the field gradient originating from ionic charges in crystals. No X-ray crystal analysis has ever been performed on potassium selenocyanates.

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