The Pure Nuclear Electric Quadrupole Resonance of N^{14} in Three Molecular Solids*

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By using an rf spectrometer[1] of the regenerative type, the pure quadrupole resonance of N^{14} has been observed in three solids: cyanogen iodide, cyanogen bromide, and hexamethylenetetramine. An "on-off" square wave of magnetic field at 280 cps was applied to the sample. In this way, the resonance was smeared out for half of the modulation period and 280 cps modulation of the absorption resulted. A narrow band amplifier, a phase sensitive detector, and an integrating output circuit were used and the signal was displayed on a recording meter. Figure 1 shows the recorded signal in $(CH_2)_6N_4$ at room temperature. The amplitude ratio of signal-to-noise in BrCN and ICN is only about one-tenth as large as this, as a result mainly, of longer relaxation times and lower density of nitrogen. A ten-times longer integration time constant was used in observing these lines to compensate partially for the loss in signal intensity. Defining the width of an absorption as $[g_{\max}(\nu)]^{-1}$, where $g(\nu)$ is the normalized shape function of the line, the observed widths are 1.05 kcps, 760 cps, and 1.08 kcps for ICN, BrCN, and $(CH_2)_6N_4$, respectively.

The frequencies were measured at room, ice, dry ice, and liquid N_2 temperatures and these data are given in Table I.

TABLE I. Frequency (Mcps) *vs* temperature.

Temperature	$(CH_2)_6N_4$	$BrC{\equiv}N$	$IC{\equiv}N$
−196°C	3.4076 ∓0.0001	(1) 2.5109∓0.0001 (2) 2.5203∓0.0001	—
− 74°C	3.3560 ∓0.0001	(1) 2.4910∓0.0002 (2) 2.4963∓0.0002	2.5512∓0.0002
0°C	3.31990∓0.00005	2.4734∓0.0002	2.5451∓0.0002
Room temp.	3.3062 ∓0.0001	(1) 2.4650∓0.0002 (2) 2.4627∓0.0002	2.5424∓0.0002
	(26.6°C)	(24.2°C)	(26.8°C)

A search over the range 2.52–2.57 Mcps failed to detect the absorption in ICN at liquid N_2 temperature. While warming up from this temperature, the crystal grains appeared to fracture violently just below dry ice temperature, possibly evidence of a phase change, and associated strains may have so broadened the line that it was undetectable. In BrCN, two lines of approximately equal intensity were observed. They have different temperature dependences and cross at 0°C. This could result if there were two nonequivalent molecules per unit cell or if there were a temperature dependent asymmetry factor $\eta=[(\partial^2V/\partial x^2)-(\partial^2V/\partial y^2)]/(\partial^2V/\partial z^2)$. For $I=1$, departure from axial symmetry would remove the $m_I=\pm1$ degeneracy and two lines would result. No data on crystal structure for BrCN has been found in the literature. Neither of the above sources of doubling of the N^{14} resonance would be present if the unit cell were similar to the unimolecular rhombohedral cell of ICN.[2] Information on this point could be obtained by observation of the Zeeman pattern in a single crystal.[3] In the gas state, quadrupole coupling constants e^2qQ/h of 3.83 ±0.08 and 3.80 Mcps are reported for BrCN[4] and ICN[5], respectively. For $I=1$, the resonance is at $\nu=\frac{3}{4}e^2qQ/h$ and the coupling constants are thus about 12 percent smaller in the solid than in the gaseous state.

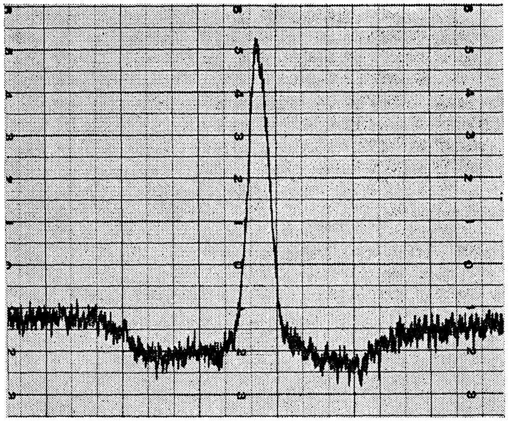

FIG. 1. Pure quadrupole absorption of N^{14} in $(CH_2)_6N_4$. The negative deflections in the wings correspond to the absorption when the modulating magnetic field is on. Each of the two cascaded *RC* integrating circuits has a time constant of 2 sec.

Relaxation times were measured by the saturation method and for ICN, BrCN, and $(CH_2)_6N_4$ they are, at 0°C, 7.4 sec, 2.7 sec, and 0.17 sec, respectively. For samples of the size used (2.5 cm^3) and these relaxation times, the rf voltages at the coil for optimum signal-to-noise are 0.19 v(rms), 0.26 v(rms), and 1.6 v(rms), respectively. At these levels, the noise figure of the spectrometer is low,[1] and little could be gained by the use of more complicated detection systems.

The relaxation time in $(CH_2)_6N_4$ was found to be 1.7 sec at −74°C and 11 sec at −196°C. If we assume the model of Bayer,[6] in which the relaxation mechanism arises from the torsional oscillations of the molecule as a whole, a dependence $T_1 \sim \tau_a T^{-1}$ is predicted, where τ_a is the average lifetime of the various states of torsional oscillation. This is not compatible with the rapid temperature dependence of T_1 that is observed unless τ_a varies with temperature.

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The Photodissociation of the Deuteron by High Energy Gamma-Rays

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An analysis was made of proton tracks found in photographic emulsions exposed to the secondary particles from a high pressure deuterium gas target bombarded by the synchrotron bremsstrahlung gamma-rays of maximum energy 320 Mev,[1] with the object of investigating the photodissociation of the deuteron in the high energy region. The secondary particles were collimated by slit systems in such a manner that we could analyze the protons at emission angles of approximately 45, 90, and 135 degrees.

The minimum energy required for a proton to penetrate through the walls of the target chamber to reach the plates was 70 Mev at 45 and 135 degrees and 60 Mev at 90 degrees. This circumstance excluded the possibility of recoil protons ejected by the photomeson producing process from reaching the plates. The energy of the proton was computed from the thickness of the absorbing material between the end point of the proton and the target.

In the case of the photo-dissociation of a deuteron into a proton and a neutron, there is a relation $k=2T[1-(T/M)(P\cos\theta/M)]^{-1}$ between the energy T and momentum P of the proton of mass M,