

INVESTIGATIONS IN NQR SPECTROSCOPY

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NQR Spectroscopy refers to that branch of spectroscopy in which energy is absorbed by various atomic nuclei in the region from ~ 1 -1000 Mc/s. A full and excellent discussion of all the theoretical and experimental aspects of the subject has been given by Semin¹. Among the more important nuclei which show the effect are Cl^{37} , Cl^{35} , Br^{81} , Br^{79} , I^{127} , Sb^{121} , Sb^{123} , Al^{27} , N^{14} , Ga^{69} , Ga^{71} , and V^{51} ; in all 131 isotopes can absorb RF energy.

The precise position of the absorption depends upon the electron density about the nucleus and the number of allowed absorption bands upon the nuclear spin. In general with nuclei of spin $3/2$, one line will be observed from each chemically distinguishable nucleus. Thus with Cl^{35} , spin $3/2$, Table I summarizes the number of bands to be expected in the indicated structures.

TABLE I

<u>STRUCTURE</u>	<u>ABSORPTION BANDS</u>
	1
	1
	2
	3

Until recently nqr spectra could be obtained only with considerable difficulty due to the wide range of frequencies over which any particular isotope might absorb (50-100 Mc/s) and the slowness of search due to the frequent necessity of adjusting the oscillators used. The instrument developed by Peterson and Bridenbaugh² has made a dramatic difference in the ease of search over wide ranges by an essentially automatic and unattended spectrometer.

In addition to the components customarily present in an oscillator of the superregenerative sort, the Peterson instrument contains an electro-mechanical servo loop which serves to stabilize the oscillator over wide ranges by feeding back a voltage to the grid of the oscillator tube, customarily a 12AU7, which results in a stabilized output at constant noise. Thus, searches are readily conducted over ranges of 20-40 Mc/s which contain the vast majority of organo chloro compound absorption bands, or 200-300 Mc/s which contain the vast majority of organo bromo compounds; the time required for such searches is 2 to 4 hours.

Some additional refinements to the Peterson spectrometer have been noted by Graybeal³, but full details on relative performance have not been published.

Previous examination of the quantitative aspects of nqr spectroscopy has largely been limited to determination of the effect of impurities on the peak intensities of absorption bands⁴ with minor references to the utility of peak intensities to determine the relative numbers of chemically different nuclei present in a molecule⁵⁻⁶. Relatively minor references will be noted in papers concerned with nqr spectroscopy with regard to sample size. It is apparent from papers containing absorption data on large numbers of compounds¹⁻⁷ that while chemical shifts comparable in principle to those observed in nmr spectra are present, splittings due to the effects of neighboring atoms are not present.

Unfortunately, a type of splitting is encountered which has to do with the fact that spectra can be determined only upon crystalline solids and is designated crystal splitting. It is due to the fact that chemically equivalent nuclei in a crystalline lattice may be physically non equivalent by virtue of relative lattice positions. Normally, it can be recognized by the extent of the splitting ~ 0.2 Mc/s, and the equal intensities of the two bands⁸. In certain cases it simplifies the interpretation of a spectrum for it has been found that virtually all trichloromethyl groups show a trio of bands of equal intensity separated by about 0.1-0.2 Mc/s.

Examination of mixtures of p-dichlorobenzene and p-dibromobenzene along the lines noted by Dean⁹ give very similar results using the Wilks Scientific Corporation NQR-1A NQR Spectrometer. Additional examples of p-dichlorobenzene and γ -hexachlorocyclohexane indicates that the peak height is an excellent way to determine the concentration of impurities present in a crystal of a chloro compound in the range from 0.01 to 1.0%, and that calibration curves of the sort generally useful in quantitative infrared measurements can easily be constructed.

With regard to the amount of sample required it has been found that employing the NQR-1A it is possible to determine usable spectra of p-dichlorobenzene on samples of 25-50 mg., although routinely 500mg will suffice for any unknown. It has been found that in general a much smaller sample, 100mg, routinely suffices for any bromo compounds where the absorption frequencies are much higher, while compounds that absorb at frequencies near 5 Mc/s will require 1000mg routinely for detection.

Careful examination of a number of spectra of diverse types of organic chloro compounds makes it apparent that nqr spectra can be used to determine the relative numbers of the different types of chloro atoms present. It has been found that peak height alone is sufficient to this end and that integration of the area is unnecessary. Thus, with 2,4-dichlorophenoxy acetic acid we find two bands of matched intensity, Spectrum 1. A molecule of γ -hexachlorocyclohexane is known to contain 3 axial and 3 equatorial chloro atoms, and due to their spatial arrangement there are effectively 4 types of chloro atoms present. The spectrum shows 4 lines of a 1:2:2:1 peak height relationship which fits the known structure¹⁰.

Unfortunately, instruments of the Peterson type cannot be used routinely for the measurement of the spectra of nitrogen compounds due to saturation phenomena precisely encountered in other types of resonance measurements. The use of other types of oscillators such as the Robinson or P-K-W oscillator¹¹⁻¹² can furnish data on many types of nitrogen compounds.

At the present time there are relatively few examples in the literature of the use of nqr to determine the structure of an organic molecule; Kozima has

used this technique to differentiate between the chlorination products of cyclohexane, 2,2-dichlorocyclohexane and 2,6-dichlorocyclohexaneone¹³.

Application of the nqr technique to γ -hexachlorocyclohexane has been noted above. A similar study of β -1,2,3,4,5,6-hexachlorocyclohexane revealed that only a single strong band is observed near 37.0 Mc/s. This agrees with the known structure in which the chloro atoms are all trans and all possess the equatorial configuration. It is of interest to note that the only easily attained isomer of 1,2,3,4,5,6-hexabromocyclohexane has a very complex spectrum and is clearly not related to the β -chloro isomer above.

γ -1,2,3,4-tetrachloro - 1,2,3,4-tetrahydronaphthalene has been the subject of a recent nmr investigation¹⁴ and has the configuration noted symbolically below:



An nqr spectrum of this compound shows two bands of equal intensity at 35 and 36.5 Mc/s and is in agreement with the nmr assignment.

The nqr spectrum of 2,4-dichlorobenzotrichloride, Formula I, might be expected to show three bands representing the three types of chloro atoms

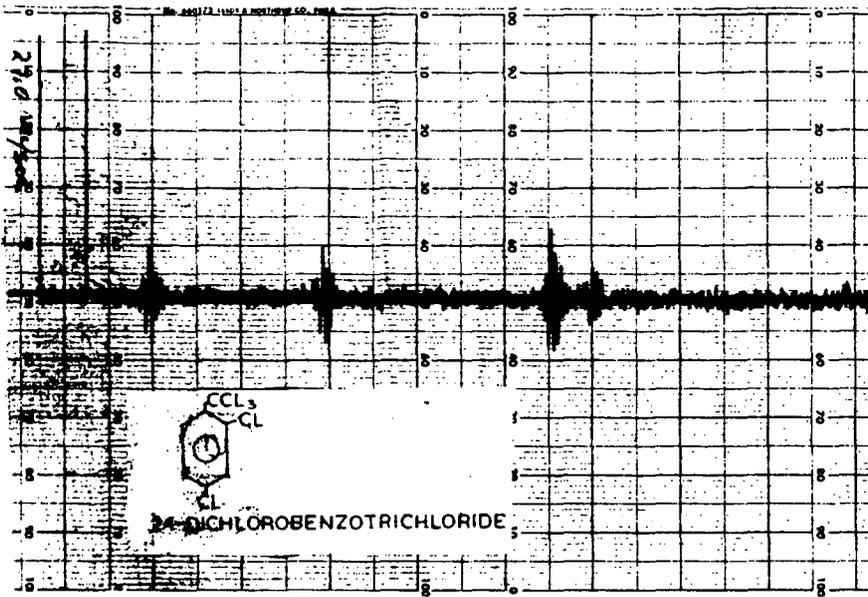


present in a 1:1:3 intensity, with probable splitting of the band due to the trichloromethyl group into a triplet. The actual spectrum (Spectrum 2) shows the expected 3 bands, however, the band at 39.0 Mc/s which is due to CCl_3 is split into a distinct doublet at a 2:1 intensity. A reasonable interpretation of this effect is that the ortho chloro group is interfering sterically with the free rotation of the trichloromethyl group. As a result of this the two chloro atoms of the trichloromethyl group nearer the ortho chloro group are different from the one which is farther.

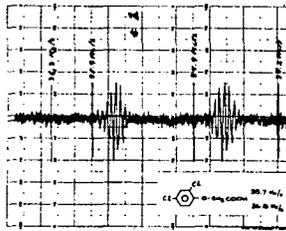
If collection of data of the sort in references 1 to 7 are studied, it is possible to develop correlation charts of the Colthrup type which have proved so popular in infrared spectroscopy. In such a chart it will be noted that in the case of organic chloro compounds that a range of 30-55 Mc/s embraces virtually all classes of chloro compounds. Acid chlorides show bands near 30 Mc/s while N-chloro compounds lie at the other end of the range near 55 Mc/s. Aromatic and aliphatic chloro compounds absorb near 34-35 Mc/s for the simple types while the more highly substituted types absorb at higher frequencies, for example; the trichloromethyl group near 39Mc/s. Spectra of compounds containing as many as 5 chemically different chloro atoms have shown five distinct bands.

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SPECTRUM 1



SPECTRUM 2