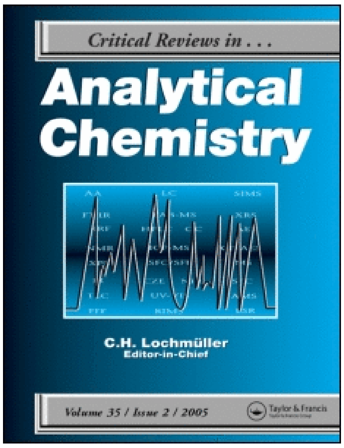


Critical Reviews in Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713400837

Theory and Analytical Applications of Nuclear Quadrupole Resonance Spectroscopy

G. Brame Edward Jr; J. D. Graybeal

To cite this Article Edward Jr, G. Brame and Graybeal, J. D.(1973) 'Theory and Analytical Applications of Nuclear Quadrupole Resonance Spectroscopy', Critical Reviews in Analytical Chemistry, 3: 3, 243 — 270

To link to this Article: DOI: 10.1080/10408347308542662

URL: http://dx.doi.org/10.1080/10408347308542662

THEORY AND ANALYTICAL APPLICATIONS OF NUCLEAR QUADRUPOLE RESONANCE SPECTROSCOPY

Author: **Edward G. Brame, Jr.**
Elastomer Chemicals Department
E. I. du Pont de Nemours & Co.
Wilmington, Del.

Referee: *J. D. Graybeal*
Department of Chemistry
Virginia Polytechnic Institute and
State University
Blacksburg, Va.

TABLE OF CONTENTS

INTRODUCTION

It has been more than 22 years from the time of the discovery of pure nuclear quadrupole resonance spectroscopy.[1B] Since that time the technique has found increased use by scientists in both physics and chemistry for studies dealing with materials in the solid state. Up to a few years ago it was primarily a physicist's tool.[1A] Various studies were performed to measure such things as the effect of pressure and temperature on the nuclear quadrupole resonance signal. However, in the last several years it has become more of a chemist's tool[2A] and has been used in those analytical applications where it can be used uniquely. It is these kinds of applications that will be covered in this review but before proceeding with that some of the theory will be covered in an elementary way. Then some of the different kinds of instrumentation that can be employed in the examination of materials that give nuclear quadrupole resonance signals will be discussed.

THE PRINCIPLES OF NUCLEAR QUADRUPOLE RESONANCE

Nuclear quadrupole resonance (NQR) is based on the interaction of the electric field gradient, q, with the quadrupole moment, Q, which is a measure of the departure of the mean distribution of nuclear charge from spherical symmetry.[2B,3B,4B,5B,6B] Figure 1 illustrates a nonspherical nucleus in an electrical field gradient. The axis of spin of the spinning nucleus can be either along the elongated direction of the nucleus or along its shortened direction. If it is along the elongated direction of the nucleus, it is defined as +Q. If it is spinning about the shortened direction of the nucleus, it is defined as −Q. However, any given nucleus is either one or the other but not both. The proton charge is defined as e and the average electric field gradient along the z-axis of the principal axis system is defined as q. The axis of quantization for the energy level distribution is defined in the direction of the electric field gradient. The strength of the interaction between the spinning nucleus and the electric field gradient is defined as the quadrupole coupling constant which is the product of the quadrupole moment, the proton charge, and the average electric field gradient, or eQq (e^2Qq is also used by some but the dimensions of q are different for this case). In detecting nuclear quadrupole resonance signals the observed line frequencies are related to the quadrupole coupling constants. As a result, the magnitude of the nuclear quadrupole coupling constant, eQq (or e^2 Qq), can often be determined directly from the line frequency.

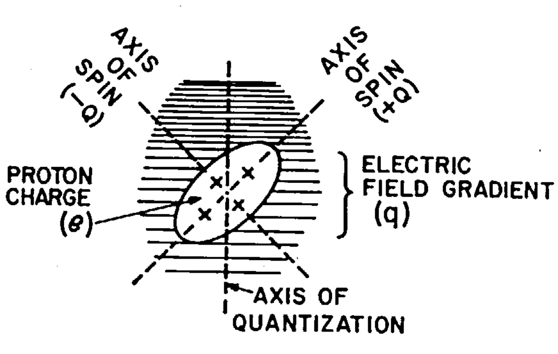


FIGURE 1. Physical description of the nonspherical spinning nucleus (Q) and its interaction with the electric field gradient (q).

Of the 103 elements in the periodic chart, 70 elements have at least one isotope that has a quadrupole moment (Q). In Figure 2 the periodic chart of elements is shown to illustrate which elements show NQR signals and which do not. There are three kinds of symbols on this chart. If there are no diagonal lines crossing the symbol of an element, each of the isotopes of that element shows an NQR signal. If there is one diagonal line crossing the symbol of an element, some but not all of the isotopes of that element show an NQR signal. Finally, if there are two diagonal lines crossing the symbol of an element, none of the isotopes of that element shows an NQR signal. From this chart it can be seen that many of the lower atomic number elements do exhibit NQR signals from one or more of their isotopes. Some of these are lithium, beryllium, boron, nitrogen, sodium, magnesium, aluminum, sulfur, and chlorine. Of those mentioned, nitrogen and chlorine have been shown the greatest interest in investigations by workers in NQR. NMR has been employed to study the resonances of these two elements as well. However, the NMR investigations have been very difficult. In order to obtain useful NMR information the principal isotope of nitrogen (^{14}N) is difficult to use, because it has a quadrupole moment and therefore gives relatively broad lines in the NMR spectrum. The ^{15}N isotope does not have a quadrupole moment and

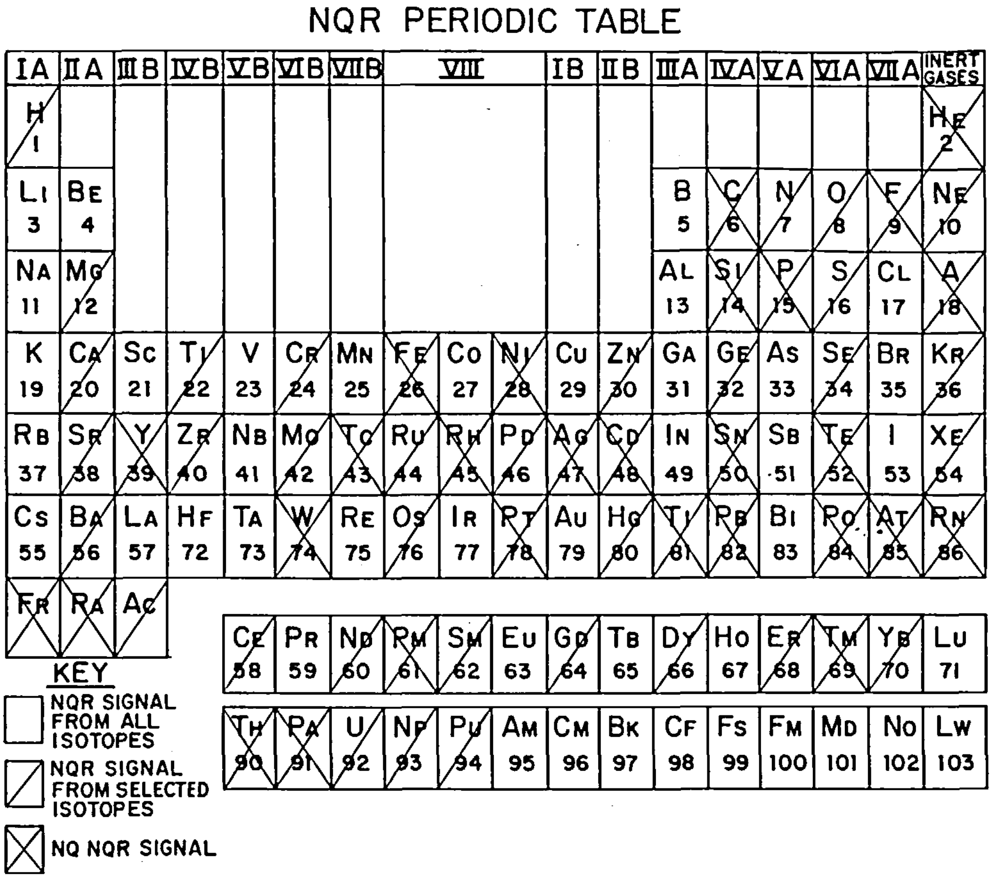


FIGURE 2. Periodic table of elements illustrating those isotopes that have quadrupole moments. (Courtesy of Wilks Scientific Co.)

can be investigated easily by NMR, but its natural abundance is only about 0.4%, and therefore its resonance is very difficult to detect. Only with the use of sophisticated computer techniques, including Fourier transform methods, can its resonances be detected. Like ^{14}N, the two principal isotopes of chlorine (^{35}Cl and ^{37}Cl) have quadrupole moments, and consequently it is often difficult to observe their NMR signals. However, for NQR measurements the resonance signals from chlorine are very easy to detect. The reason for this difference between NMR and NQR can be seen from Figure 3. In this figure, the energy level diagram is shown for the case of the nucleus with a spin quantum number of 3/2. Since both the ^{35}Cl and ^{37}Cl isotopes have spin quantum numbers of 3/2, this energy level diagram fits the situation for chlorine in NMR and NQR. The resonance condition for NMR involves the separation of energy levels by a magnetic field (H_0). When the magnetic field is equal to zero, no resonance is observed in the NMR experiment. However, when the magnetic field is not equal to zero, there is a separation of the energy levels into four levels.

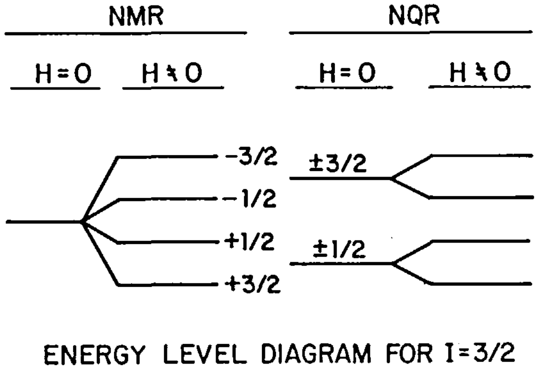
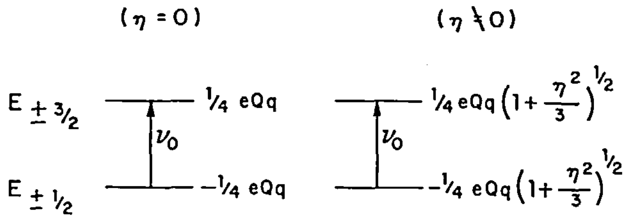


FIGURE 3. Comparison of the energy level diagram between NMR and NQR for a nuclear spin of 3/2.



ENERGY LEVEL DIAGRAM FOR I = 3/2 (H=0)

FIGURE 4. Comparison of the energy level diagram between asymmetry parameters of 0 and greater than 0 for a nuclear spin of 3/2.

Then, as a result of this type of energy level separation, for example, several transitions occur for a single kind of chlorine. In essence, this is one of the factors which cause broad lines to occur in the NMR experiment. The other is that the T_1 relaxation time is short. In NQR, however, when the applied magnetic field is zero, there are two energy levels for material in the solid state. The lower energy level of $M_I = \pm 1/2$ and the higher energy level of $M_I = \pm 3/2$ allow only one transition to occur for each kind of chlorine in the compound. If a weak magnetic field is applied to the sample under NQR examination both the lower and the higher energy levels are separated with a resulting line broadening and at least two lines for each kind of chlorine possibly appearing. In analytical work it is important that the experiment produce as simple a spectrum as possible in order to be able to use line frequency information and to correlate it with structure. Thus, in the case of the NQR experiment a weak magnetic field is generally not used unless certain kinds of information such as exact quadrupole coupling constants and asymmetry parameters are desired. As a result of these considerations it is seen why NQR is preferred over NMR for observing resonance signals from those isotopes that have spin quantum numbers of 3/2.

In contrast to high-resolution NMR which is performed in a liquid or solution state, NQR is performed in the solid state. Thus, the averaging effect that occurs in the high-resolution NMR experiment is not observed in the NQR experiment. As a result the nuclear spin system in its interaction with the electric field gradient is sensitive to bond orientation. This sensitivity to bond orientation occurs because of the contribution of electrons in the bond to the tensor components and to the effect of neighboring ions and/or molecules in the crystal. There are three field gradient tensor components (q_{zz}, q_{yy}, and q_{xx}) in a three-dimensional Cartesian coordinate system. The principal field gradient tensor component is q_{zz}, which is along the principal axis of quantization. Thus, from these field gradient tensor components, a quantity called the asymmetry parameter η is defined. It is equal to $(q_{xx} - q_{yy})/q_{zz}$. This parameter, η, can vary from zero to one. When η is equal to zero, there is axial symmetry about the z-axis direction. When η is equal to one, there is only a two-dimensional gradient effect. Frequently η is expressed in percent between 0 and 100%.

Taking this new parameter η into account, the energy level diagram for a spin of 3/2 at zero magnetic field strength is shown in Figure 4. First, when η is equal to zero the energy levels are $E_{\pm 1/2}$ for the lower level and $E_{\pm 3/2}$ for the upper level. One transition is observed at ν_0. Then, for η not equal to zero, again two energy levels are seen with a resultant single transition. For this latter case the quadrupole coupling constant (eQq) is not simply related to the transition frequency. It is so related only when η is equal to zero. In this latter case η must be known or defined in order to determine the quadrupole coupling constant from the resonance frequency of a given type of, for example, chlorine. For many chlorine compounds η is either zero or nearly so.

Fortunately this is most often the case with organic compounds. However, for inorganic compounds the situation may be completely different in that η may have a significant value and may actually contribute some useful information to the structural determination of the material under study.

Because as indicated above, nitrogen is one of the more important of the elements that can be examined by NQR, we now turn our attention to a theoretical consideration of energy level

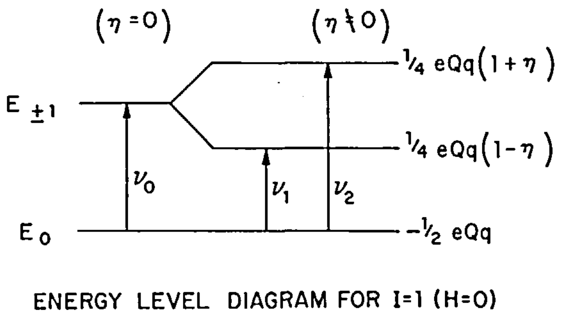


FIGURE 5. Comparison of the energy level diagrams between asymmetry parameters of 0 and greater than 0 for nuclear spin of 1.

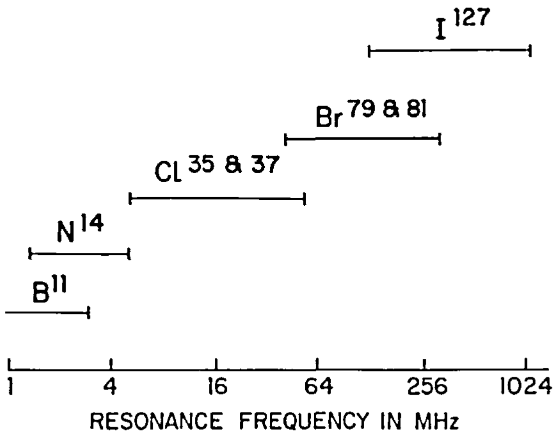


FIGURE 6. Correlation chart of frequency with the more important isotopes that have quadrupole moments.

diagrams for isotopes such as ^{14}N with a spin quantum number of one. In Figure 5, we show the energy level diagram for such an isotope. The two cases mentioned above for isotopes having a spin quantum number of 3/2 are also indicated here. When η is equal to zero we see that there are two energy levels of zero and ±1 with a single transition frequency ν_0. However, for the case when η is not equal to zero there are three energy levels. These give rise to two transitions ν_1 and ν_2. The relationship between these transition frequencies and the quadrupole coupling constant (eQq) is seen to depend on the asymmetry parameter η. The magnitude of η determines the degree of separation of the two upper energy levels. The greater the separation the greater the separation of the two transition frequencies ν_1 and ν_2. Thus, we see from this energy level diagram that, for those isotopes that have a spin quantum number of 1, by measuring the frequency of transition at ν_1 and the frequency of the transition at ν_2, both the quadrupole coupling constant (eQq) and the asymmetry parameter (η) can be determined readily. This ease with which the asymmetry parameter can be determined for spin systems of 1 is contrasted with the difficulties for the spin system mentioned previously where the spin quantum number was 3/2. Then since most nitrogen-containing groups are unspherically bonded with nonaxial symmetry, the asymmetry parameter for these nitrogen atoms is generally much greater than zero. Thus, the asymmetry parameter, which can be determined experimentally in a straightforward manner, can be used as a kind of correlation parameter for structure determination. This parameter, of course, can be used in conjunction with the quadrupole coupling constant and the experimentally measured transition frequencies for the structure determination of a given kind of nitrogen. Thus, by using the two frequencies observed, both unknowns, the quadrupole coupling constant eQq and the asymmetry parameter η can be calculated very easily for use in structure studies.

Even though our discussion thus far has concentrated on a few of the most important isotopes that can be measured in nuclear quadrupole resonance spectroscopy, many of the other 70 or more isotopes can also be studied very easily by NQR.[7B,2A] Some of these, in addition to nitrogen and chlorine, are included in Figure 6. They include ^{11}B, ^{79}Br, ^{81}Br, and ^{127}I. Just the examination of the nuclear quadrupole resonance of these seven different isotopes covers a range in frequency from below 1 MHz to more than 1,000 MHz or 1 GHz. Thus, it can be seen very readily from the large frequency range over which nuclear resonance signals can be observed why it is difficult to design equipment that can not only scan the frequency range of interest but do so under essentially high-resolution conditions. The advantage of the NMR experiment over the NQR experiment is that the magnetic field which must be used by NMR can be varied over a wide range of field strengths so as to minimize the frequency range employed. In NQR the use of the magnetic field only serves to split and broaden lines and to decrease the resolution of lines that are obtained. There are two different approaches that can be used to improve sensitivity in the NQR spectrum. One is instrumental; the other is by computer techniques. By varying the temperature and/or the pressure of the sample under examination with appropriate instrumental hardware, significant improvements in sensitivity can be achieved. Also, by computer techniques such as signal averaging or long term filtering significant improvements in sensitivity can be achieved. In addition to sensitivity improvement, there is an important temperature effect in a shift of the frequency of the resonance lines in the NQR spectrum. This shift in the resonance signal with temperature has been used by some workers as a method to use NQR for the measurement of temperature.

INSTRUMENTATION

Because pure nuclear quadrupole resonance frequencies cover a range from 10^6 to 10^9 Hz, a broad range of the electromagnetic frequency spectrum often must be examined in order to find nuclear quadrupole resonance signals. This long-range searching required for obtaining pure quadrupole resonance signals requires instrumentation that is capable of covering this whole frequency spectrum. Over the years since nuclear quadrupole resonance was first detected, there are basically three kinds of instrumentation that have emerged. They can be grouped into the following categories: (1) continuous wave oscillators, (2) periodically quenched oscillators, and (3) oscillators whose frequencies can be pulsed at varying but regularly spaced intervals. Included in the first category is the simple oscillator recognized independently by Roberts[1C] and Pound.[2C,3C] This simple oscillator had been used previously for detection of NMR signals. When the oscillator is stable and does not require continuous attention, searches can be made very slowly. As a result, the narrow band detection system employed by the instrument can be used to yield good sensitivities for the detection of nuclear quadrupole signals.[4C] The search for unknown resonances must frequently be made over a range anywhere from several MHz to more than ten MHz. Because of the large range that must be covered in obtaining nuclear quadrupole resonance signals and the generally narrow width of the absorption lines that can be observed, a single sweep of the frequency range can take as long as several hours to even a day. This long length of time required to sweep the frequency spectrum severely limits the utility of this first instrumental approach to the detection and measurement of NQR frequencies. Nevertheless, this type of instrument has advantages in the accurate measurement of line frequency and line shape.

A schematic diagram of a commercial oscillator[5C] employing a continuous wave oscillation for detection of NQR signals is shown in Figure 7. This regenerative oscillator instrument is designed to cover the frequency range from about 2 MHz to about 50 MHz. It was produced commercially for a few years but has been discontinued. Since the range covered by this instrument includes the range of frequencies where ^{35}Cl and ^{37}Cl resonances appear, it was used almost exclusively for measurement of these resonances. The oscillator-detector system first used by Knight to detect quadrupole signals was modified in the development of this instrument. The modification involved the substitution of frequency modulation for Zeeman modulation and the use of a difference amplifier to cancel the incidental amplitude modulation that often results from frequency modulation. The cancellation is accomplished by using a reference signal from the same 280 Hz tuning fork oscillator that is used to frequency modulate the oscillator-detector. The signal from the difference amplifier is amplified and detected with a lock-in detector that is also referenced to the same 280 Hz tuning fork oscillator. Then, the DC signal from the lock-in detector is used to provide the error signal for locking the spectrometer to a quadrupole resonance. The output from the lock-in detector is a signal resembling a derivative that can be seen in Figure 8 for the ^{35}Cl resonance of $KClO_3$. This signal is typical of that which is obtained from spectrometers that operate with frequency modulation of magnetic fields. Its appearance is identical to that of spectra obtained from ESR and wide line NMR spectrometers. Since this instrument is capable of obtaining resonance signals over the range from nearly 2 MHz to about 50 MHz, ^{14}N signals can also be observed with it. Nearly all the early work on ^{14}N resonances has been done with this instrument. That is mainly because the radio frequency power levels can be adjusted more accurately with this instrument than with the periodically quenched oscillator instrument. Signal and noise characteristics for this instrument have been analyzed.[6C] Varian has a wide line NMR instrument that can be used for the NQR examination but it is far more limited in operation than any of the others.

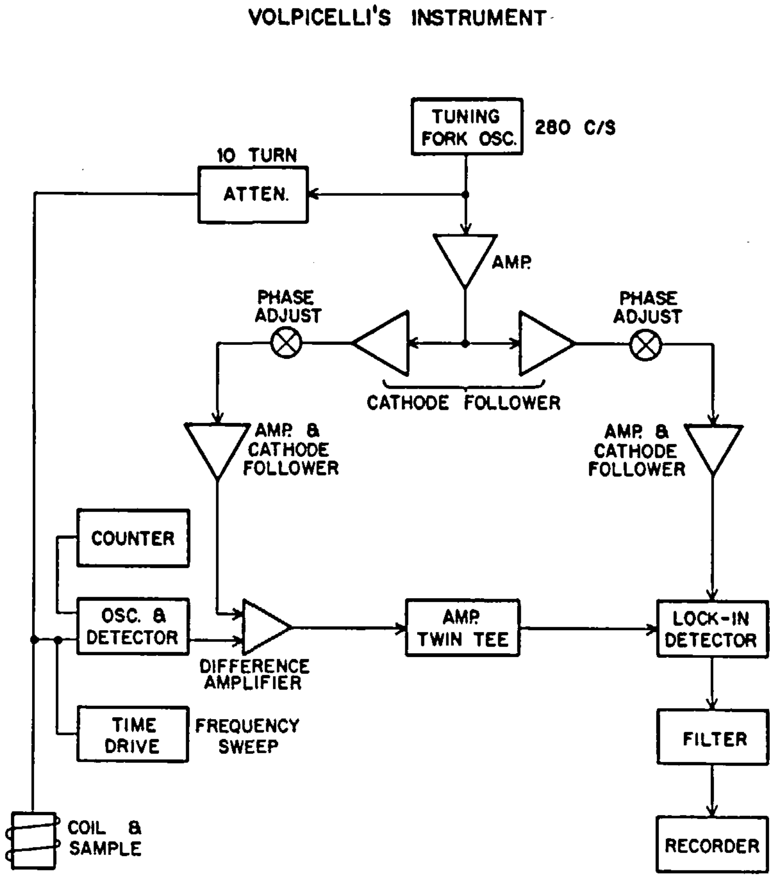


FIGURE 7. Regenerative oscillator-detector NQR instrument following the design of Volpicelli et al. (Courtesy of *Rev. Sci. Instrum.*, 36, 150 (1965).)

The second type of instrument that can be used for detecting NQR signals is the super-regenerative oscillator-detector. This type of instrument was first used by Dehmelt[7C] more than 15 years ago to detect NQR signals. Since that time many investigators have employed this instrument to detect NQR signals and measure their frequencies. In fact, nearly all the investigators have worked with this type of instrument rather than the other two kinds primarily because of its apparent ease for detecting quadrupole resonance signals. About eight years ago, Dr. G. E. Peterson of the Bell Telephone Laboratories developed the first automatic spectrometer[8C] for measuring these NQR signals. He used the basic design of a super-regenerative instrument and incorporated into it a feedback loop to vary the quench frequency of the oscillator in order to cause the coherence of the oscillator to be varied with frequency of scan for maintaining constant noise output. Figure 9 shows

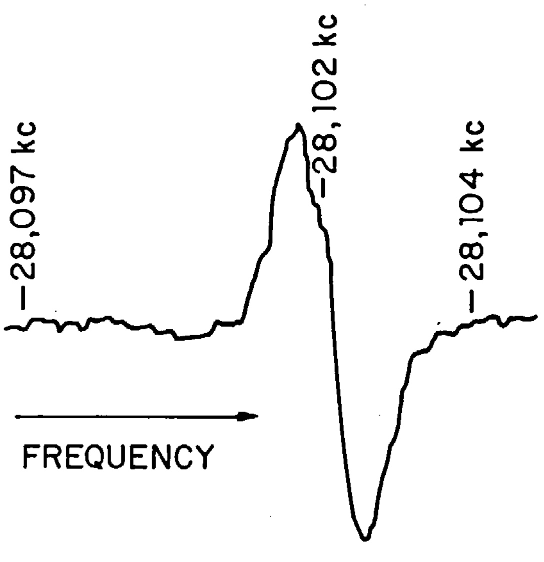


FIGURE 8. ^{35}Cl resonance signal of KClO$_3$ from the regenerative oscillator-detector instrument.

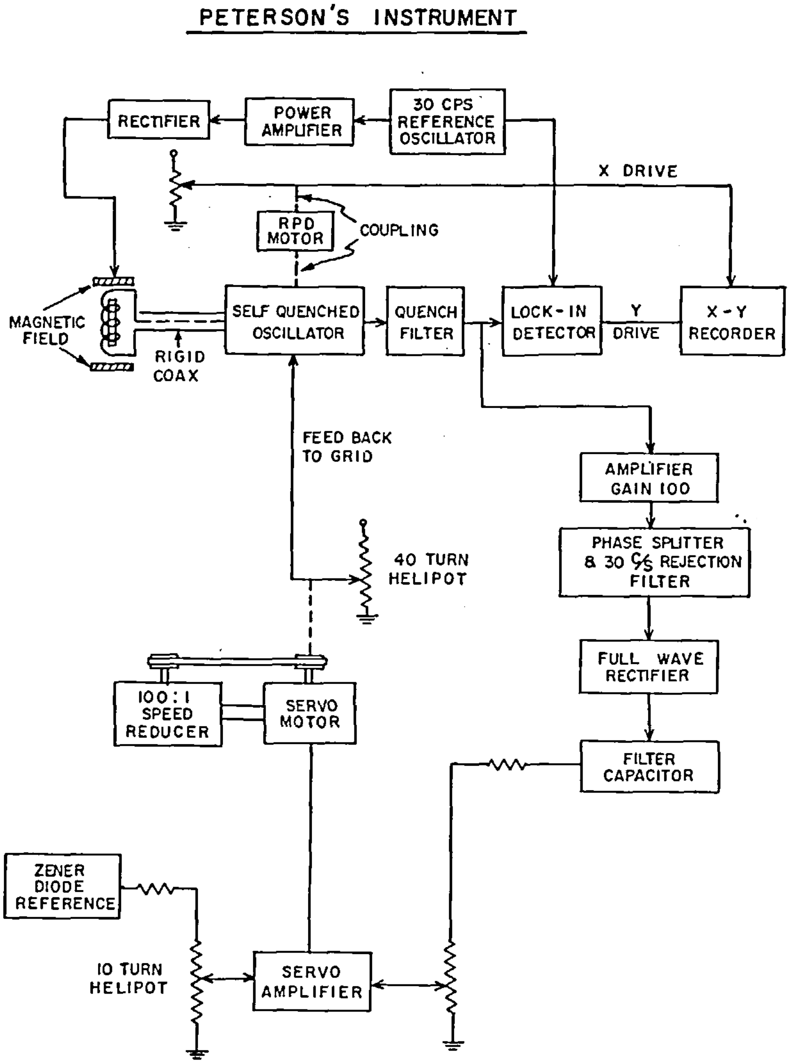


FIGURE 9. Super-regenerative oscillator-detector NQR instrument following the design of Petersen et al. (Courtesy of *Rev. Sci. Instrum.*, 35, 6, 698 (1964).)

a schematic diagram of this instrument. In addition to the self-quenched oscillator, quench filter, and lock-in detector arrangement, we see from the diagram that the output from the quench filter is fed into an amplifier, phase splitter, full wave rectifier, and then a filter capacitor before being compared to a zener diode reference through a servo amplifier. Thus, as the carrier frequency is varied, the signal being compared with the zener diode reference is also varied. The result in the difference of signal voltage with respect to the voltage of the zener diode is to change the feedback voltage of the grid bias in the oscillator-detector. This change is handled through a servo-motor, pulley system, and a 40-turn Helipot that is supplied with about 325 V d.c. Instead of frequency-modulating the carrier frequency, Zeeman modulation can also be used with this kind of spectrometer. Zeeman modulation involves the use of a pair of Helmholtz coils that are mounted around the sample coil. A 30 Hz reference audio oscillator is used to supply the alternating current to these coils. However, the alternating current is rectified by a half-wave rectifier so that only half of the alternating current cycle reaches the coil. This modulation frequency is also referenced to a lock-in detector which relates it to the modulation signal. The output is

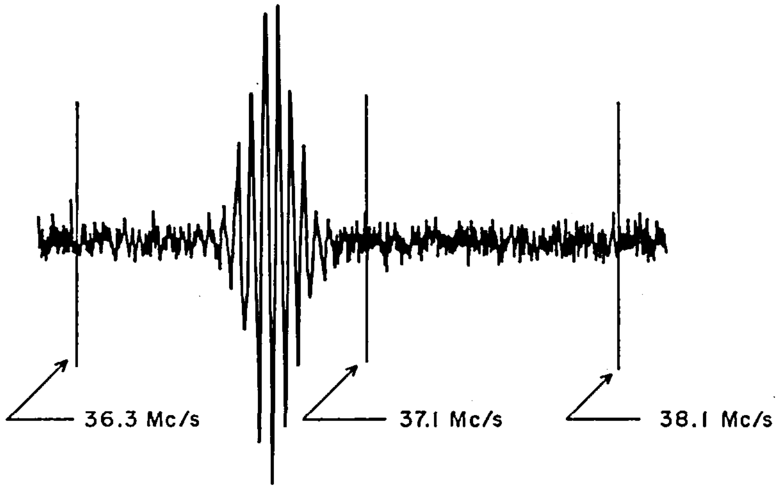


FIGURE 10. ^{35}Cl resonance signal of the β-isomer of 1,2,3,4,5,6-hexachlorocyclohexane from the super-regenerative oscillator-detector instrument. (Courtesy of *Anal. Chem.*, 39, 918 (1967).)

fed to an x-y recorder for spectral presentation. A typical signal obtained on this instrument is shown in Figure 10. It was obtained from the resonance of the β-isomer of 1,2,3,4,5,6-hexachlorocyclohexane. The chief distinction between this signal and the signal obtained from the previously discussed regenerative oscillator-detector instrument is that it shows multiplet fine structure. The multiplet structure arises from the quenching of the super-regenerative oscillator during frequency scanning. This turning on and off of the oscillator causes beat patterns to form; the separation of these beats in frequency is directly proportional to the quench frequency. Because of the appearance of these beats it is often difficult to determine the center band frequency. Lines can overlap each other if there is more than one line near each other. The beat pattern can also be asymmetric, instead of being reasonably symmetrical as it is in Figure 10, and its asymmetry can then interfere in the interpretation of the spectral pattern.

There are several manufacturers of super-regenerative oscillator-detectors. They include Wilks Scientific Co. of South Norwalk, Conn., and Decca-Radar Ltd. of England. The Wilks Scientific version is a completely transistorized model of the instrument first developed by Peterson a number of years ago. It is designated as model NQR-1-A. The range of frequencies it covers is from about 5 MHz to more than 200 MHz. Thus, it includes all the chlorine resonances and nearly all the bromine resonances in its range of detectability.

The Decca-Radar Ltd. spectrometer is based primarily on the instrument developed by Dr. J. A. S. Smith[9C,10C] of the University of London. The principal features of this instrument are (1) its wide frequency scan (about 2 MHz to more than 60 MHz), (2) automatic sideband suppression of the beat pattern that appears as a result of the super-regenerative oscillator system, (3) automatic gain control, and (4) marker frequencies to indicate the frequency of the carrier throughout the scan. The automatic sideband suppression technique and the method used to calibrate the frequency are the unique features of this particular instrument. As a result, with their use, this instrument clearly is superior to other super-regenerative commercial instruments currently available and operating in the frequency range of from about 2 to 60 MHz. Anyone interested in building his own inexpensive unit can follow the leads provided by several workers in the field.[11C,12C]

The third type of NQR instrument is the pulse or spin echo apparatus. It was developed by Hahn[1A] and used by him for obtaining nuclear quadrupole resonance information. In addition, there is a group at the National Academy of Sciences of the USSR at Moscow[13C,14C,15C,16C] engaged in performing pulse experiments to obtain quadrupole resonance information. Also, a dissertation on an operating pulse system is available to anyone interested in constructing one for his own work.[17C] Hahn has used the pulse system for obtaining quadrupole frequencies of alkali-metal nuclei. These frequencies occur around 1 MHz or more. As a result of their frequencies being very low in relationship to other quadrupole resonances in the radio frequency portion of the spectrum, they could not have been detected by either the regenerative oscillator-detector or the super-regenerative oscillator-detector systems. At present there is only one commercial pulse spectrometer available. It is manufactured by Bruker Scientific Co., Burlington, Mass. The model number of this pulse spectrometer is SXP 2-200. It operates over a frequency range from about 2 to 200 MHz and is useful for measuring relaxation times T_2*, T_2, and T_1. In addition, it can be used to perform the Fourier transform of the free induction decay following a 90° pulse near the frequency of any of the isotopes that produce a resonance in the frequency range 2 to 200 MHz. Besides obtaining relaxation times and spectral data, the principal advantage of this pulse method is the saving of time that it makes possible in acquiring spectral data. Since the main disadvantage of NQR spectroscopy is the time that is consumed in searching for unknown resonance signals, the pulse method can save a considerable amount of time, perhaps even as much as 90% of what is required by the other two instrumental methods discussed. Other advantages of the pulse technique include: (1) an accurate determination of small line splittings which may arise from spin coupling interactions or strong magnetic dipolar couplings between neighbors, (2) improved accuracy in locating the principal components of the electric field gradient and the calculation of the asymmetry parameter in the presence of inhomogeneous broadening, and (3) the observation of resonance signals from those nuclear resonances, such as ^{14}N, that saturate easily under continuous wave (C.W.) operation (which the other instrumental methods use).

The instrumentation discussed thus far has involved primarily the detection of resonances in the frequency range from 2 to about 200 MHz. Since the ^{35}Cl and ^{37}Cl resonances appear within this range, obviously they have been at the center of interest in instrument development. In order to detect resonances at frequencies outside this range modifications of existing instruments are required. For the detection of ^{127}I resonances (which appear in the range from 300 to about 1,000 MHz) the modifications include: (1) a high-frequency triode which drives a loaded transmission line,[18C] (2) a push-pull circuit designed to operate in the range from 200 to 700 MHz,[14C] (3) a special LC-oscillator designed to operate in the range from 200 to 400 MHz,[14C] and (4) an externally quenched super-regenerator with square-wave Zeeman modulation designed to operate between 250 and 610 MHz.[14C]

APPLICATIONS

To date there have been very few applications of NQR spectroscopy to analytical determinations. However, there are some correlations which have been developed on a limited basis to show that correlation charts like those used extensively in infrared and NMR spectroscopy can also be used in NQR spectroscopy. However, because temperature affects the resonance frequency of the NQR signal[5C] a constant reference temperature must be used in any correlation studies. The reference temperature normally used in NQR studies is −196°C (liquid nitrogen temperature). This temperature was chosen because (1) it is readily attainable and (2) it can be used for many materials that are liquid at room temperature but freeze to a solid crystalline form at this low temperature.

Some quantitative studies have been worked out with NQR spectroscopy but these applications have been very limited in scope and have been applicable primarily to inorganic materials rather than to organic materials. The reasons for the difficulties in performing a quantitative analysis by NQR on organic solids will be discussed in a later section.

Qualitative

^{35}Cl *Resonances*

In the qualitative use of NQR spectroscopy, it is apparent that correlation charts developed from studies of model compounds must be used in order to relate signals from an unknown spectrum with the structural features of the material showing that spectrum. Thus, charts[1D] like the one shown in Figure 11 can be of great help in relating unknown signals to structure. This chart shows a correlation

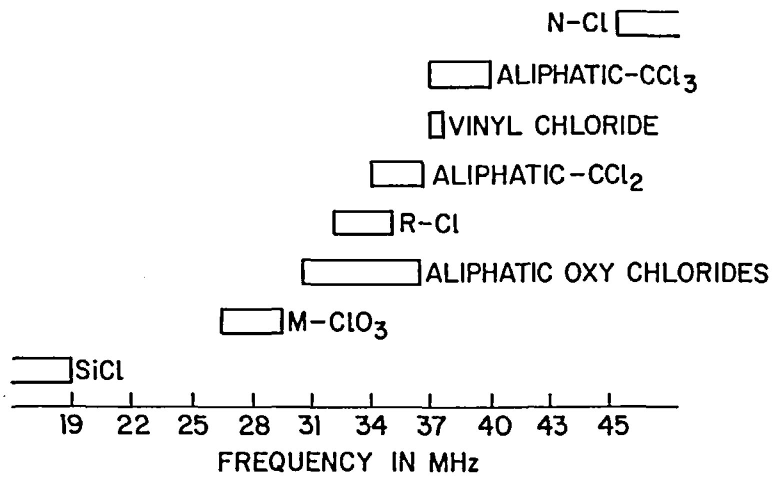


FIGURE 11. Correlation chart of ^{35}Cl resonance frequencies, obtained at –196°C, with structure for chlorine-containing compounds. (Courtesy of *Anal. Chem.*, 39, 918 (1967).)

of frequencies at –196°C with structure for ^{35}Cl resonances in the frequency range from about 16 MHz to about 50 MHz. It is within this range that nearly all chlorine-containing organic compounds show their ^{35}Cl resonances. Chlorine-containing inorganic compounds can, and often do, give ^{35}Cl resonances outside this range of frequencies. However, from the figure it is seen that signals of Si-Cl groups appear at the low end of the frequency region. Then, except for metal chlorates, the remainder of the frequency range over which ^{35}Cl signals appear is between 30 and 40 MHz. Here, we see signals from aliphatic oxychloride, R-CCl, R-CCl$_2$, and R-CCl$_3$ groups. From this figure it is also seen that the crowding of chlorines from CCl and CCl$_3$ groups causes the resonances to shift to higher frequencies in about the same way that the crowding of fluorines from CF to CF$_3$ groups causes resonances to shift in ^{19}F NMR spectra. This relationship is seen in light of the fact that most ^{35}Cl resonance signals from organic compounds have line widths about 2 KHz and that the frequency range over which most of these resonance signals occurs is about 10 MHz. Thus, the ratio of range to signal width for ^{35}Cl resonances is about 5,000 to 1. This ratio is equivalent to about the best possible resolution one can obtain in a high-resolution NMR spectrometer for proton spectra. In other words, it would be equivalent to a line width of about 0.2 Hz in a range of 1,000 Hz which is the normal range for observing proton resonances. The disadvantage of NQR is that in order to observe unknown resonances with line widths of 2 KHz over a frequency range of 2 MHz the amount of time required can be the order of several hours or more with either the regenerative or super-regenerative instruments. This kind of operation is in sharp contrast to that normally performed by high-resolution NMR. However, with the use of a pulse NQR spectrometer that disadvantage of the long use of instrument times may very well be overcome.

A more detailed correlation [1D] of the different types of chlorines in aliphatic compounds is shown in Figure 12. The data shown in this correlation

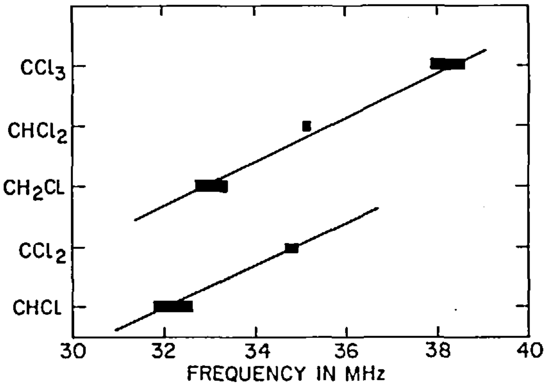


FIGURE 12. Correlation chart of ^{35}Cl resonance frequencies, obtained at –196°C, with structure for chlorine-containing aliphatic groups. (Courtesy of *Anal. Chem.*, 39, 918 (1967).)

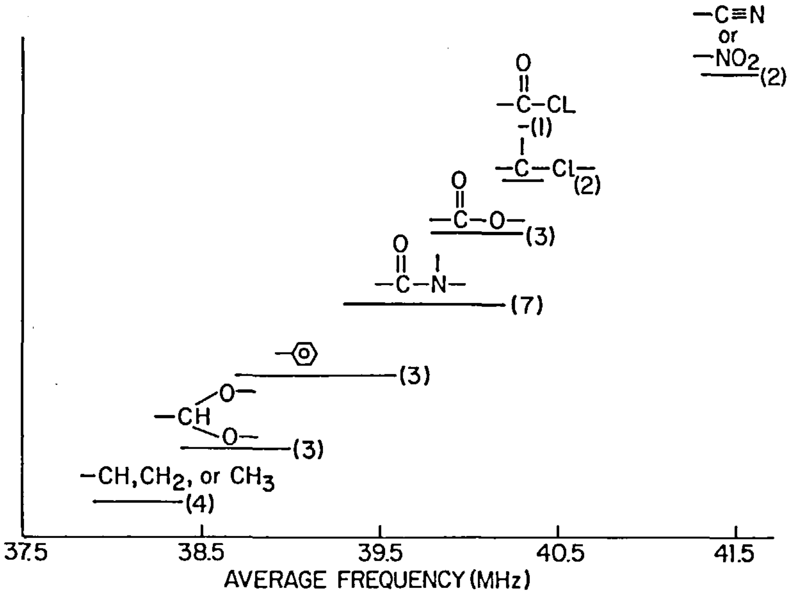


FIGURE 13. Correlation chart of ^{35}Cl resonance frequencies, obtained at −196°C, for CCl_3 groups with varying kinds of adjacent structure groups. (Courtesy of *Anal. Chem.*, 43, 35 (1971).)

chart were obtained at −196°C. There are two parallel lines showing the correlation of the resonance frequency, between about 32 MHz and 39 MHz, with the structural groups shown on the ordinate axis. Since the two correlation lines are essentially parallel, it is seen that the replacement of a hydrogen by a chlorine shifts the quadrupole resonance frequency by about the same amount regardless of whether the substitution takes place in an end group or along the chain of the organic compound. It is further seen that CCl_3 groups appear at the highest frequencies (about 40 MHz) for carbon-chlorine groups.

An even more detailed correlation chart[2D] of structure groups with quadrupole resonance frequency is shown in Figure 13. This correlation involves the effect of varying the group adjacent to a CCl_3 group on the quadrupole resonance of CCl_3 groups. Here we find a variation in the shift between about 38 MHz to about 41 MHz with eight different kinds of structure groups attached to CCl_3 groups. From this figure, we see that the quadrupole resonance frequency for a CCl_3 group in an aliphatic compound is in the neighborhood of about 38 MHz and is very little dependent on whether the CCl_3 group is attached to a CH, CH_2, or CH_3 group. However, on replacing any of these groups with any of the other groups shown in this correlation chart, the CCl_3 group average frequency shifts to higher frequencies. Thus, for NO_2 or nitrile groups we find that the average CCl_3 quadrupole resonance fequency is shifted more than about 3 MHz, to nearly 41 MHz. This serves to illustrate the fact that the quadrupole resonance frequency of CCl_3 groups at liquid nitrogen temperature can be very sensitive to the adjacent groups. In Figure 14 a correlation[3D] is shown between the quadrupole resonance frequencies of the CCl_3 and $CClH_2$ groups and the number N of methylene groups intervening between them. As the number of methylene groups increases, the resonant frequency of the CCl_3 group decreases at first, and then becomes constant if N equals or exceeds about 4. Similar behavior is observed for the $CClH_2$ group: The resonance frequency for the chlorine of this group decreases as the number of intervening methylene groups increases up to about 4; then it remains the same as the number of these methylene groups increases further. However, there is a more dramatic change in the resonance frequency for the $CClH_2$ group than for the CCl_3 group. There is a shift in frequency of about 3 MHz for the $CClH_2$ group but only about 1 MHz for the CCl_3 group. Thus, the

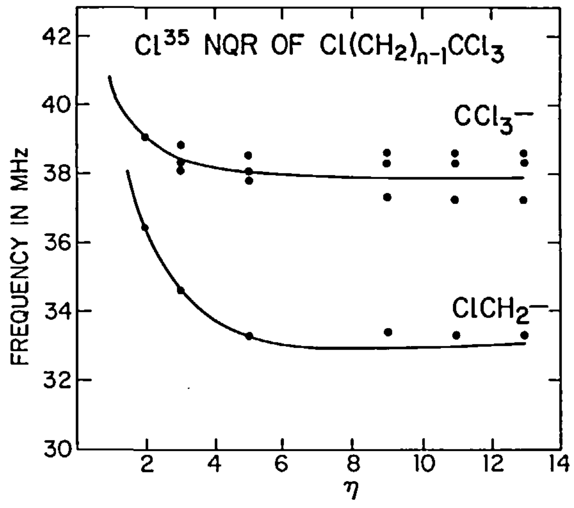


FIGURE 14. Correlation of ^{35}Cl resonance frequencies, obtained at −196°C, for CCl_3 and $CClH_2$ groups with varying number of intervening methylene groups. (Courtesy of *Zh. Strukt. Khim.*, 7, 1, 117 (1966).)

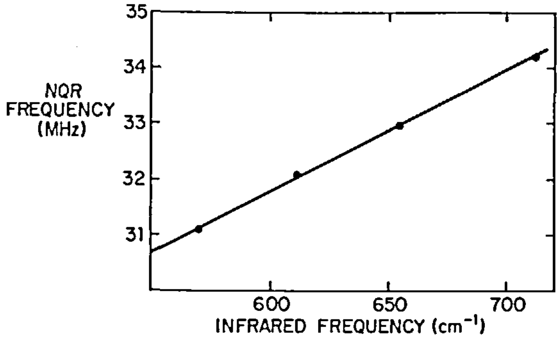


FIGURE 15. Correlation of ^{35}Cl resonance frequency of alkyl chlorine-containing groups with the infrared frequency of the carbon-chlorine stretching vibration. (Courtesy of *Nature*, 212, 922 (1966).)

correlation illustrates the effect of relatively minor changes in structure of organic compounds on the quadrupole resonance frequencies of chlorine-containing groups.

In addition to the kinds of spectra structure correlations discussed above, several others have been shown to exist for the quadrupole resonance frequency of various isotopes. One of these correlations shows the relationship between the quadrupole resonance frequency of a chlorine-containing group and the frequency of the infrared vibration.[4D] It is shown in Figure 15. Here we see that there is a direct correlation between shift in the NQR frequency and the shift in infrared frequency for the carbon-chlorine stretching vibration. The shift in the NQR frequency is seen to be about 3 MHz for this correlation whereas the shift in the infrared spectrum is about 150 wavenumbers. As is seen in the figure, there is an essentially linear correlation between the NQR results and the infrared results. Other correlations reported show the relationship between the NQR frequency and (1) Hammett's σ constant,[5D,6D] (2) various bonding parameters,[7D,8D] and (3) various kinds of spectroscopic data including infrared, Raman, and x-ray data.[9D-11D] Thus, with the use of correlation charts such as those described herein, unknown ^{35}Cl spectra can be interpreted in terms of structure for structural determinations. Of course, in addition to relating the observed frequencies to structure groups through correlations, the number of lines observed for a given compound can be used in making a more complete structural interpretation. However, care must be taken in counting lines and relating each line to a given nuclear resonance because of the effect of multiple unit cell sites in causing "crystal splitting" of lines. The splittings due to nonequivalent crystallographic sites often can amount to as much as several hundred KHz. They frequently can be distinguished by experienced workers from other nuclear resonances because the two or more signals arising from the splitting for each nuclear resonance are usually equal in intensity and in line separation. Area ratios can be used whenever there are two or more lines for relating the relative intensities of these lines to each other so that the relative number of different kinds of chlorines in the compound can be determined. A number of articles containing relatively large amounts of quadrupole resonance data for ^{35}Cl have appeared in the literature. Certain collections, such as the NQR bibliography published by Wilks Scientific Corp.,[8B,9B] are useful in attempting to identify certain structural groups. It is data like those given in these collections that will permit NQR spectroscopy to become as important and useful in its applications to chemical problems as other areas of spectroscopy, such as infrared, mass spectroscopy, and NMR are today.

^{14}*N Resonances*

The isotope that is showing the greatest promise for NQR measurements is ^{14}N since nitrogen-containing compounds are generally more plentiful than any of the other compounds that have quadrupole moments. The techniques, such as infrared, mass spectroscopy, and NMR, that are being used to determine the structures of nitrogen-containing compounds are generally inadequate. High-resolution NMR with Fourier transform equipment shows promise in the examination of the low abundant ^{15}N isotope (0.365%) because this has a spherical nucleus and no quadrupole moment. Infrared spectroscopy can be used to determine the presence of certain nitrogen groups but it frequently has its limitations. Mass spectroscopy can often be used effectively in determining the different structural groups in which nitrogen is contained. However, it is frequently ineffective with regard to high-molecular-weight compounds. Nuclear quadrupole resonance spectroscopy, on the other hand, could be one of the most important analytical tools for use in determining the structures of nitrogen-containing compounds. Not only can NQR detect the highly abundant (99.6%) ^{14}N isotope in various nitrogen-containing materials, but it can also be used to measure the degree of bond asymmetry about the nitrogen nuclei. Thus, measurements of both the quadrupole resonance frequency and the asymmetry parameter can be used in correlations with structure. Figure 16 shows a correlation chart prepared from nitrogen resonance data reported in the literature.[1D] Nine different structural groups are correlated in this chart. The frequency range covered is from about 2.3 MHz to about 4 MHz. Line widths observed for signals in the nitrogen resonance frequency range are generally less than 1 KHz. This chart shows several trends that can be useful in structure determination. The most significant is the relationship between C≡N, C=N, and C–N, and frequency. As the bond length of a carbon-nitrogen bond is increased, as it is in passing from a C≡N to a C–N group, the ^{14}N resonance frequency is seen to increase. Another trend is seen for the different types of primary amines. The average resonance frequency is smaller for N–N bonds than for C–N bonds, and the frequency for nitrogen in ammonia lies between these. Thus, it is seen from this figure that these spectra structure correlations can be helpful as a primary aid in the structure determination of unknown materials containing nitrogen. If a nitrogen-containing structure group cannot be identified with certainty by means of a frequency correlation chart such as this one, then perhaps with the use of the asymmetry parameter a determination can be made.

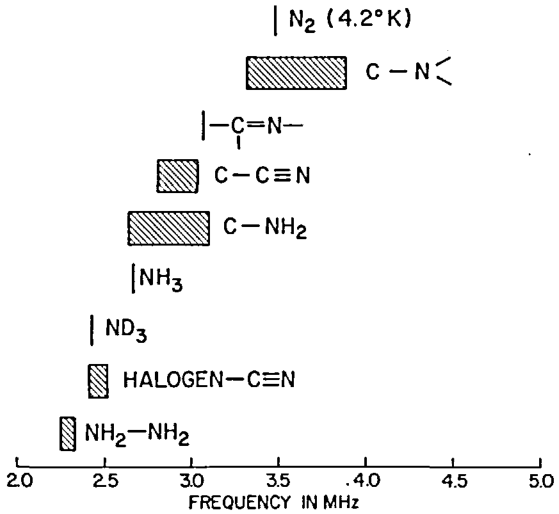


FIGURE 16. Correlation chart of ^{14}N resonance frequencies, obtained at –196°C, with nine different structure groups for nitrogen-containing compounds. (Courtesy of *Anal. Chem.*, 39, 918 (1967).)

Up to a few years ago there had been only a few ^{14}N quadrupole resonances observed. There were several reasons why this was so. First, the ^{14}N resonances occur in the low-frequency portion of the radio frequency spectrum. Second, because the spin quantum number of nitrogen is one, there are usually at least two resonance lines for each kind of nitrogen in the compound. Third, the ^{14}N resonances of certain nitrogen-containing groups are saturated very easily. As a result of this saturation problem it is impossible to detect the nitrogen resonance signal under certain conditions. More recently, the knowledge of the problems associated with detecting ^{14}N resonances has made it possible to observe more resonances and to report the data obtained in the literature. Table I is a compilation of the data reported in the literature for various kinds of nitrogen-containing groups. The table is divided into eight columns. The first column gives the structure of the compound. The second column indicates the temperature that was used in obtaining the data. The third column gives the resonance frequencies observed in MHz. For those cases in which the nitrogen has axial symmetry, only one resonance

TABLE 1

^{14}N Nuclear Quadrupole Resonance Data

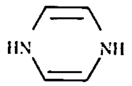
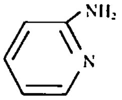
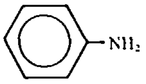
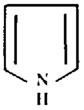
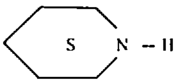
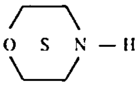
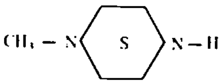
Sample	Temperature, °K	ν_{reson} (MHz)	eQq/h (MHz)	η%	T_1 (sec)	T_2* (sec)	Ref.
Amines							
NH_3	77	2.3706	3.1607	0			5E
ND_3	77	2.4230	3.2307				5E
$NH_3 \cdot 1/2\ H_2O$	77	2.3862	3.1698	1.1			28E
		2.3105					
		2.3685					
		2.2682	3.0524	2.7			
H_2NNH_2	77	4.6109	4.821	82.8			11E
		4.5606	4.819	78.6			
		2.6717					
		2.6170					
		1.9950					
		1.8910					
CH_3NH_2	77	3.3622	3.986	37.4			18E, 21E
		2.6117					
$(CH_3)_2NH$	77	3.8308					
		3.0940					
		3.8805	4.662	33.0			18E, 21E
		3.1118	4.618				
$(CH_3)_3N$	77	3.8954	5.194	0			18E, 21E
$C_2H_5NH_2$	77	3.3593	4.0592	30.9			21E
		2.7296					
$(C_2H_5)_2NH$	77	3.644	4.6181	24.5			21E
		3.103					
		3.2843	4.0560	24.5			
		2.7210					
C_4H_9NH	77	3.3898	4.0539	34.5			29E
		2.6912					
$(C_2H_4)_3N_2$	78.8	3.693			16.5		15E
	290.2	3.658			0.1		
$(CH_2CH_2)_3N_4$	77	3.407			17.0		7E
	292.5	3.310			0.02		
	300	3.6035	4.413	26.6	0.1	1.2×10^{-3}	9E
		3.0161			0.0075	0.6×10^{-3}	
	77	2.970	3.550	34.65			16E
		2.355					
	77	3.243	3.932	26.9			16E
		2.720					
	77	1.685	2.062	26.88			14E
		1.408					
	77	3.6668	4.4313	31.0			23E
		2.9802					
	77	3.6630	4.4822	26.8			23E
		3.0603					
	77	3.6824	4.4524	30.0			23E
		3.0256					

TABLE 1 (continued)

^{14}N Nuclear Quadrupole Resonance Data

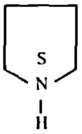
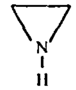
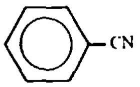
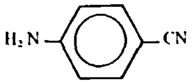
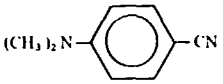
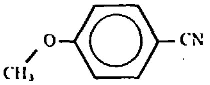
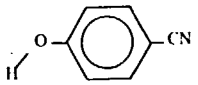
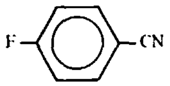
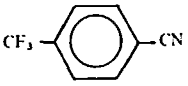
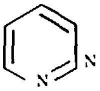
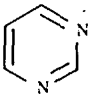
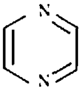
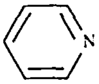
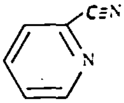
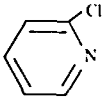
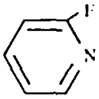
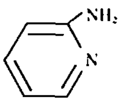
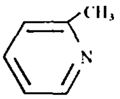
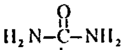
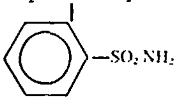
Sample	Temperature, °K	ν_{reson} (MHz)	eQq/h (MHz)	η%	T_1 (sec)	T_2* (sec)	Ref.
	77	3.6380 2.9016	4.3597	33.8			23E
	77	3.1578 2.2185 3.1473 2.2068	3.56	52.5			24E, 25E
Nitriles							
$K_2Zn(CN)_4$	77	3.1042	4.1390	0			17E
$K_2Cd(CN)_4$	77	3.1491	4.1988	0			17E
$K_2Hg(CN)_4$	77	3.0694 3.0414 3.0356	4.0739 4.0475	1.37 0			17E
$Hg(CN)_2$	77	2.9945 2.9325	3.9513	3.14			17E
HCN	77	3.0223 3.0052	4.0183	8.5			3E
CH_3CN	77	2.8078 2.7992	3.738	4.6	~0.2		1, 27E
CCl_3CN	77	3.0444 3.0337	4.0521	0.53			2E
$CH_2(CN)_2$	77	3.0154 2.8670	3.9216	7.57			1E
C_2H_5CN	77	2.8513 2.8121	3.7756	2.08			1E
CH_2ClCN	77	3.0582 2.7832	3.8943	14.1			4E
	77	3.0183 2.8098	3.8854	10.73			2E
4-$C_5H_4N(CN)$	77	2.9353 2.9073	3.8951	1.44			2E
2-$C_5H_4N(CN)$	77	3.0396 2.8978	3.9583	7.16			2E, 20E
	77	3.0155 2.9253	3.9605	4.55			26E
	77	3.0192 2.8840	3.9355	6.87			26E
	77	2.9730 2.8648	3.8919	5.56			26E
	77	3.0183 2.8098	3.8854	10.73			26E
	77	2.9763 2.7633	3.8264	11.13			26E
	77	2.9932 2.5662	3.7063	23.04			26E

TABLE 1 (continued)

^{14}N Nuclear Quadrupole Resonance Data

Sample	Temperature, °K	ν_{reson} (MHz)	eQq/h (MHz)	η%	T_1 (sec)	T_2* (sec)	Ref.
Nitrites							
$NaNO_2$ (Ferroelectric)	77		5.792	40.5			22E
$Ba(NO_2)_2 \cdot H_2O$	77	3.69 3.68 4.67 4.65					19E
Heterocyclics							
	77	4.01176 3.99302 3.78026 3.77773	5.18892	8.53			12E
	77	3.75796 3.75244 2.90036 2.89789	4.43621	38.6			12E
	77	4.29448 2.99226 1.30246	4.85783	53.6			12E
	77	3.892 2.984	4.584	39.6			12E, 20E
	77	3.948 3.130	4.718	34.66			16E, 20E
	77	3.627 3.051	4.452	25.86			16E, 20E
	77	3.399 2.904	4.202	23.63			20E
	77	2.842 2.776	3.745	3.5			4E
	77	3.713 2.975	4.458	33.1			16E
Thiocyanates							
CH_3SCN	77	3.0524 2.2207	3.5154	47.32			10E
C_2H_5-SCN	77	3.1178 2.2677	3.5903	47.35			10E
$NCSC_2H_4SCN$	77	3.0726 2.2446	3.5448	46.71			10E
Amides							
 $H_2N-\overset{O}{\overset{\|}{C}}-NH_2$	77	2.91336 2.34784	3.50746	32.24	78 40	1.6×10^{-3} 9.5×10^{-4}	8E
	90	3.172	4.229	0			13E
Miscellaneous							
NF_3	35	5.11 5.06		1.4			6E

line is expected and only one is reported. For those compounds in which the nitrogen does not have axial bond symmetry, at least two resonance frequencies are reported. In some cases three or more lines are reported. The number of lines may exceed three because of the "crystal splitting" effect which is often observed in NQR spectra. The fourth column gives the quadrupole coupling constant in MHz. The quadrupole coupling constant is calculated from the relationship of the observed frequencies to the difference between them. Whenever the asymmetry parameter is zero, there is a simple relationship between the observed frequency and the quadrupole coupling constant. However, when the asymmetry parameter significantly exceeds zero two or more lines are observed and the relationship is not simple, but there the asymmetry parameter can be calculated along with the quadrupole coupling constant. The fifth column shows the asymmetry parameter, η, calculated from the observed frequencies. This asymmetry parameter can be seen to vary considerably from compound to compound. For example, for ammonia the asymmetry parameter is zero, and the same is true for trimethylamine. However, for monomethylamine and dimethylamine it is very different from zero: 37% for monomethylamine and 33% for dimethylamine. The next two columns give, whenever available, the relaxation times, T_1 and T_2*. The values of both are given in seconds. It is seen that the relaxation time, T_1, varies greatly with temperature. For example, for hexamethylenetetramine $T_1 = 17.0$ sec at −196°C, whereas at about room temperature T_1 is seen to be 0.02 sec. Thus, the large difference in the value of T_1 between liquid nitrogen temperature and ambient temperature (about a factor of 10^3 for a temperature variation of about 200°C) illustrates the large sensitivity that T_1 can have with temperature. In addition to the correlations involving the asymmetry parameter, there appear to be some useful correlations involving T_2. The fact that the relaxation time T_1 is very high for urea is most significant. It is about 80 sec for the upper resonance line and about 40 sec for the lower resonance line at liquid nitrogen temperature. The values for T_2* are much shorter. Because of the fact that line saturation is proportional to $\gamma^2 H_1{}^2 T_1 T_2$, it can be seen very readily why those lines that have relatively high T_1 values can be saturated with lower H_1 power levels than those with low T_1 values. Only by working at low power levels of the radio frequency field (H_1) can the effect of high T_1 values be minimized in causing saturation of quadrupole resonance signals. The last column lists the literature references for the data given in the table. This table is then seen to be divided into seven different structural categories. They include amines, nitriles, nitrites, heterocyclics, thiocyanates, amides, and one example of a miscellaneous kind of compound.

Upon close examination of the data in Table 1 a number of correlations appear other than those mentioned already that can be helpful in structure determination work. For example, the value of the asymmetry parameter can very often be utilized effectively along with the observed frequencies and the calculated quadrupole coupling constants for structure determination work. In the table under the heading "heterocyclics" we see that the first three examples in order are pyridazine, pyrimidine, and pyrazine. From the observed frequencies and quadrupole coupling constants of these compounds it would be very difficult to distinguish among them. The average resonance frequency for the upper lines in these three compounds is very nearly the same. The quadrupole coupling constants of the three compounds do not vary in a straightforward way. However, on comparing the values of their experimentally determined asymmetry parameters we see that there is a significant and correlatable difference among them. Bond asymmetry is seen to increase between pyridazine and pyrazine. As a result the variation in the asymmetry parameter is about a factor of six among these three compounds. That means that the hybridization character of the sp^2 orbitals is seen to increase significantly between pyridazine and pyrazine. Nitrile groups show very low values for the ^{14}N asymmetry parameter, which is seen to vary from about zero to around 23% and to have an average of about 6 or 7%. Heterocyclics, in general, show some of the highest values for the asymmetry parameter, which for these compounds can range from about 4% up to about 54%, and which appear to be about 30% on the average. Thiocyanates, at least for the three examples shown in the table, have relatively high values of the asymmetry parameter. These all appear to be about 47%. Amides, at least for the two examples listed here, have asymmetry parameters varying from zero to 32% for their asymmetry parameter.

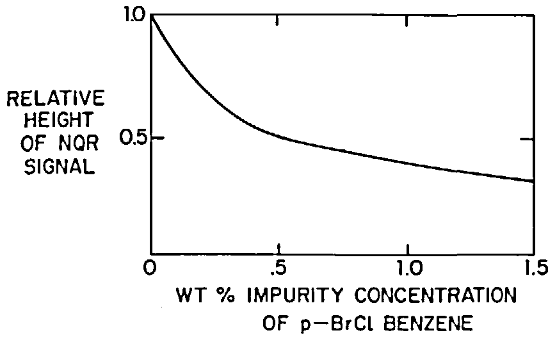


FIGURE 17. Plot of the relative height of the NQR signal of *p*-dichlorobenzene with impurity concentration of *p*-bromochlorobenzene. (Courtesy of *J. Phys. Soc. Jap.*, 13, 5, 446 (1955).)

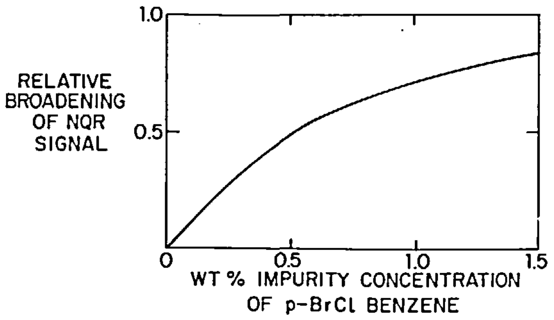


FIGURE 18. Plot of the relative broadening of the NQR signal of *p*-dichlorobenzene with impurity concentration of *p*-bromochlorobenzene. (Courtesy of *J. Phys. Soc. Jap.*, 13, 5, 446 (1955).)

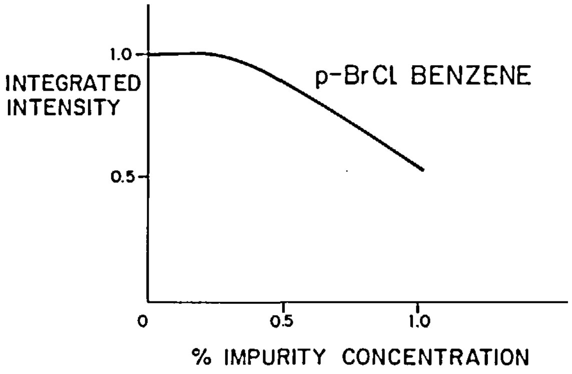


FIGURE 19. Plot of the integrated intensity of the NQR signal of *p*-dichlorobenzene with impurity concentration of *p*-bromochlorobenzene. (Courtesy of *J. Phys. Soc. Jap.*, 13, 5, 446 (1955).)

Other Nuclear Resonances

Quadrupole resonance signals from nuclei other than ^{35}Cl and ^{14}N have been observed. They include ^{79}Br, ^{81}Br, ^{127}I, ^{11}B, and a relatively large number of the transition elements. Of these it appears that ^{79}Br and ^{81}Br have been studied more than any of the others. There are data in the literature showing how the resonance frequency of bromine depends on the structure of the molecule or group containing it, but the extent of the literature in this area of investigation by nuclear quadrupole resonance spectroscopy is considerably less than for ^{35}Cl, ^{37}Cl, and ^{14}N.

Quantitative

Quantitative analysis is currently difficult to perform by nuclear quadrupole resonance spectroscopy. In the first place, the sensitivity varies with both the state of the sample and the frequency of measurement. Crystalline samples give sharper and more intense lines than glassy or semicrystalline samples. In addition, the population distribution governed by the Boltzmann factor favors the detection of resonances at higher rather than at lower frequencies. Thus, resonances occurring in the 30 to 40 MHz region are more easily detected than resonances occurring in the 2 to 4 MHz region. In the second place, the sensitivity is also a function of the level of impurities that are present in solid samples. An example of the effect of impurity on the quadrupole resonance of a sample containing chlorine is seen in Figures 17, 18, and 19. Figure 17 shows the effect of the concentration of bromochlorobenzene, present as an impurity, on the relative height of the NQR signal of *p*-dichlorobenzene.[12D] It is seen from this figure that the relative height changes most rapidly with changing concentration of impurity when that concentration is lowest (~ 0.1 to 0.5 weight %) of impurity concentration. Above a concentration of *p*-bromochlorobenzene of 0.5 weight % the slope of the curve changes to reflect the effect expected from dilution of the sample by the impurity. Figure 18 shows the effect of the concentration of *p*-bromochlorobenzene on the broadening of the NQR signal of *p*-dichlorobenzene. Here, as in the previous figure, we see that the greatest effect on the relative broadening of the NQR signal occurs at the lower concentrations of impurity. Above 0.5% impurity concentration the change in slope for the relative broadening of the NQR signal with impurity concentration reflects the dilution effect that is expected as the concentration of impurity in the sample matrix is increased. In Figure 19, the effect of the *p*-bromochlorobenzene impurity on the integrated intensity of the NQR signal of *p*-dichlorobenzene is seen. In this figure we see that the impurity has no significant effect on the integrated intensity when its concentration is small; only if the concentration of impurity exceeds about 0.3 to 0.4 weight % is there any effect seen. Thus, from the curves shown in Figures 17, 18, and 19 we see that integrated intensity measurements are preferred over peak-height measurements for determining the relative amounts of different chlorine groups in a given sample. However, for measuring impurity concentration in a given sample peak-height measurement would be preferred. Finally, we can say, on the basis of the integrated intensity results in Figure 19, that we can obtain results similar to those obtained in high-resolution NMR studies for structure analyses if the relative intensity measurements involve lines that are not separated very much in frequency from each other. If several lines that appear over a rather large frequency range have to be compared, the intensity relations may not be possible to solve. Once detectors become available with responses that are relatively constant over a large frequency range, it should be possible to perform quantitative analysis by NQR spectroscopy on almost any kind of solids in much the same way as we do currently by NMR spectroscopy on liquids.

Several years ago some quantitative measurements were made by NQR on several different kinds of inorganic materials.[13D] Calibration curves were prepared before the measurements were made. Included in these earlier calibration curves were the results shown in Figure 20. The two curves in this figure were established for the two signals from ^{35}Cl in $HgCl_2$ observed at 22.4 and 22.5 MHz. Cuprous oxide was used as the diluent. Peak intensity was measured from two resonance signals and plotted on the ordinate. Good linear relationships are seen between the peak intensities of both ^{35}Cl resonance signals and the weight of mercuric chloride in cuprous oxide. This indicates that quantitative NQR spectroscopy is also possible with careful control for inorganic materials. It must be realized and emphasized that only with careful calibration and control of the conditions being used for the analysis can quantitative NQR spectroscopy be practical. Even then it is rather apparent from the above examples that the integrated intensity measurement is the only method that can be used. Grinding of samples and incorporation of the nuclear species into different kinds of chemical compositions, such as mixtures or solid solutions, will affect the shape of the resonance line for the nuclear species being examined, but will have significantly less effect on the integrated intensity measurement. So, the integrated intensity measurement is an essential element in the quantitative analysis of NQR spectra, but calibration of the system under examination by comparison with similar samples having known contents of the species being determined also appears to be necessary if optimum quantitative results are to be obtained.

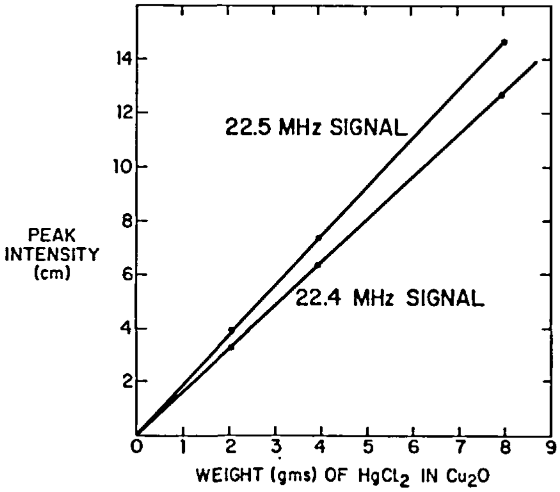


FIGURE 20. Plot of the peak intensity of the ^{35}Cl quadrupole resonance in $HgCl_2$, with Cu_2O as diluent, against the concentration of Hg_2Cl_2. (Courtesy of *Anal. Chem.*, 41, 661 (1969).)

Temperature Dependence

In general, as the temperature is lowered from ambient temperature to liquid nitrogen temperature, the NQR frequency increases. Line broadening generally does not occur. However, resonance frequencies in the ^{35}Cl range can shift by as much as 0.5 to 0.7 MHz at 35 MHz between ambient temperature and liquid nitrogen temperature (−196°C).[5C] In fact, this shift has been suggested as a sensitive method to measure temperature. Such a method was developed using the ^{35}Cl resonance signal from potassium chlorate. With this material the measurement of temperature was accurate to about ± 0.004°C.[5C] A number of workers[14D-20D] have tried to explain this effect in variation of the NQR signal with sample temperature. Most workers explain it on the basis of its relationship to changes in the crystal structure. Obviously, some crystals would change more with temperature than others and as a result their quadrupole resonances would shift more with temperature than others.

Relaxation Times

To date only a few values have been obtained for the relaxation times T_1 and T_2^*. Some of these are included in the section involving ^{14}N studies. Their possible utility was also pointed out in that section. However, aside from these studies and the results mentioned, very little information has been obtained about them for most nuclear quadrupole resonances including those of ^{35}Cl, ^{37}Cl, ^{79}Br, ^{81}Br, and ^{127}I. These values can often be used in structural determinations along with the quadrupole coupling constants and frequencies of quadrupole resonance signals. The relaxation times can also be used to gain understanding of molecular motions occurring within samples and to detect various kinds of discontinuous transitions. In obtaining values for the relaxation times T_1 and T_2^* pulse methods have been found to be the most straightforward and useful.[8E,9E] Because of the saturation problem frequently encountered in ^{14}N quadrupole resonance work, it has become more important for the study of ^{14}N resonances than for the other commonly studied nuclear quadrupole resonances such as ^{35}Cl, ^{37}Cl, ^{11}B, ^{79}Br, ^{81}Br, and ^{127}I.

REFERENCES

Books

1A. Das, T. P. and Hahn, E. L., *Nuclear Quadrupole Resonance Spectroscopy, Solid State Physics*, Academic Press, New York, 1958.
2A. Lucken, E. A. C., *Nuclear Quadrupole Coupling Constants*, Academic Press, New York, 1969.

General and Review Articles

1B. Dehmelt, H. G., Pure quadrupole resonance in solids, *Naturwissenschaften*, 37, 111 (1950).
2B. Duchesne, J., Recent applications of nuclear quadrupole resonance in structural and radiation chemistry, *J. Chem. Soc. (Lond.)*, Special Publ. No. 12, 235 (1958).
3B. Dailey, B. P., The interpretation of quadrupole spectra, *Discuss. Faraday Soc.*, 19, 255 (1955).
4B. Drago, R. S., Nuclear quadrupole resonance spectroscopy, in *Physical Methods in Inorganic Chemistry*, Van Nostrand Reinhold, New York, 1956, 315.
5B. Orville-Thomas, W. J., Nuclear quadrupole coupling and chemical bonding, *J. Chem. Soc. (Lond.)*, 11, 162 (1957).
6B. O'Konski, C. T., *Determination of Organic Structures by Physical Methods*, Vol. 2, Nachod, F. C. and Phillips, W. D., Eds., Academic Press, 1962, 661.
7B. Semin, G. K., Investigation of nuclear quadrupole resonance in the series of bromine- and iodine-containing disubstituted benzenes, *Zh. Strukt. Khim.*, 3(3), 292 (1962).
8B. Truett, W. L. and Wilks, D. K., *NQR Bibliography*, Wilks Scientific Co., 1st ed., June 1967.
9B. Wilks, D. K., *NQR Bibliography*, Wilks Scientific Co., Suppl. 1, December 1970.
10B. Biedenkapp, D. and Weiss, A., Correlations between ^{35}Cl nuclear quadrupole resonance (NQR) frequencies of chlorobenzene derivatives and characteristic reaction parameters of the substituents, *J. Chem. Phys.*, 49(9), 3933 (1968).
11B. Harrison, J. F., Nuclear quadrupole coupling constants in polyatomic molecules, *J. Chem. Phys.*, 48, 2379 (1968).
12B. Smith, J. A. S., NQR, *J. Chem. Educ.*, 48(1), 39 (1971).
13B. Smith, J. A. S., NQR-PT III chemical applications, *J. Chem. Educ.*, 48(3), A 147 (1971).
14B. Smith, J. A. S., NQR-PT III chemical applications, *J. Chem. Educ.*, 48(4), A 243 (1971).
15B. Chihara, H. and Nakamura, N., "Nuclear quadrupole resonance spectroscopy," in *Magnetic Resonance*, INTP Med. Tech. Publ. Co., Oxford (1972).
16B. Schempp, F. and Bray, P. J., Nuclear quadrupole resonance spectroscopy, in *Physical Chemistry, An Advanced Treatise*, Vol. 4, Academic Press, New York, 1970.

Instrumental Articles

1C. Roberts, A., New methods of detecting nuclear radio-frequency resonance absorption, *Rev. Sci. Instrum.*, 18, 845 (1947).

2C. Pound, R. V., Nuclear paramagnetic resonance, *Progr. Nucl. Phys.*, 2, 21 (1952).

3C. Pound, R. V. and Knight, W. D., Radio-frequency spectrograph and simple magnetic-field meter, *Rev. Sci. Instrum.*, 21, 219 (1950).

4C. Verdieck, J. F. and Cornwell, C. D., Radio-frequency spectrometer with bidirectional square wave frequency modulation, *Rev. Sci. Instrum.*, 32(12), 1383 (1961).

5C. Volpicelli, R. J., Nageswara Rao, B. D., and Baldeschwieler, J. D., A locked RF spectrometer for nuclear quadrupole resonance, *Rev. Sci. Instrum.*, 36, 150 (1965).

6C. Howling, D. H., Signal and noise characteristics of the PKW marginal oscillator spectrometer, *Rev. Sci. Instrum.*, 36(5), 660 (1965).

7C. Dehmelt, H. G. and Kruger, H., Quadrupol-Resonanz-Frequenzen Von Cl- Und Br-Kernen in Kristallinem Dichloräthylen und Methylbromid, *Z. Phys.*, 129, 401 (1951).

8C. Peterson, G. E. and Bridenbaugh, P. M., Wideband feedback coherence control for superregenerative NQR spectrometers, *Rev. Sci. Instrum.*, 35(6), 698 (1964).

9C. Smith, J. A. S. and Tong, D. A., An improved super-regenerative spectrometer for nuclear quadrupole resonance spectroscopy, *J. Sci. Instrum.*, 2, 1, 8 (1968).

10C. Smith, J. A. S., LVI. Nuclear quadrupole resonance spectroscopy. Part 2 – Instruments, *J. Chem. Educ.*, 48(2), A 77 (1971).

11C. Muha, G., Automatic coherence control for super-regenerative NQR spectrometers, *Rev. Sci. Instrum.*, 39, 416 (1968).

12C. Graybeal, J. D. and Croston, R. P., Operational amplifier control for NQR spectrometer, *Rev. Sci. Instrum.*, 38, 122 (1967).

13C. Safin, I. A., Pavlov, B. N., and Stern, D. Ya., Steady-state and pulse methods in nuclear quadrupole resonance studies, *Zavodskaya Laboratoriya*, 30(6), 676, June (1964).

14C. Grechishkin, V. S. and Soifer, G. B., Nuclear quadrupole resonance instrumentation, *Pribory i Tekhn Eksperim.*, 1, 5 (1964).

15C. Safin, I. A. and Osokin, D. Ya., Coherent pulse spectrometer for nuclear quadrupole resonance of ^{14}N, *Instr. Exp. Tech.*, 14(1), 180 (1971).

16C. Smith, J. A. S., LVI. NQR spectroscopy. Part 3 – Pulse methods; chemical applications, *J. Chem. Educ.*, 48(3), A 147 (1971).

17C. Daniel, A. C., Pulse Spectrometer, Ph.D. dissertation, University of Alabama, 1964; University Microfilms, Inc., Ann Arbor, Mich., 64–12, 777.

18C. Bridenbaugh, P. M. and Peterson, G. E., Wide band feedback coherence control for super-regenerative NQR spectrometers II, *Rev. Sci. Instrum.*, 36, 702 (1965).

Articles on Interpretation of Chlorine-containing Spectra

1D. Brame, E. G., Jr., Analytical aspects of nuclear quadrupole resonance spectroscopy, *Anal. Chem.*, 39(8), 918 (1967).

2D. Brame, E. G., Jr., Chlorine-35 nuclear quadrupole resonance studies of trichloromethyl compounds, *Anal. Chem.*, 43(1), 35 (1971).

3D. Semin, G. K. and Robas, V. I., Investigation of NQR spectra of ^{35}Cl in tetrachloroalkanes, *Zh. Strukt. Khim.*, 7(1), 117 (1966).

4D. Gerdil, R., Empirical correlation between NQR frequencies and IR absorption data, *Nature*, 212, 922 (1966).

5D. Meal, H. C., Correlation of ^{35}Cl nuclear quadrupole coupling frequencies with Hammett's sigma, *J. Am. Chem. Soc.*, 74, 6121 (1952).

6D. Bray, P. J. and Barnes, R. G., Estimates of Hammett's sigma values from quadrupole resonance studies, *J. Chem. Phys.*, 27(2), 551 (1957).

7D. Kottenbah, D. E. and Silvidi, A. A., Nuclear quadrupole resonance study of the inductive effect in chemical bonding in chloroalkenes, *J. Chem. Phys.*, 52(3), 1270 (1970).

8D. Ainbinder, N. E., Grechishkin, V. S., and Osipenko, A. N., The asymmetry parameter of the electric field gradient in molecular crystals, *Zh. Strukt. Khim.*, 7(1), 111 (1966).

9D. Stidham, H. D., Librational amptitudes: raman and nuclear quadrupole resonance spectra of *p*-dichlorobenzene and *p*-dichlorobenzene d_4, *J. Chem. Phys.*, 49(5), 2041 (1968).

10D. Barton, B. L., Rotational vibrations of pyrazine from temperature dependent ^{14}N NQR and x-ray thermal tensors, *J. Chem. Phys.*, 55(4), 1984 (1971).

11D. Barton, B. L., Assignment of librational vibrations of CH_3CCl_3 from NQR, far IR, and low frequency raman data, *J. Chem. Phys.*, 55(4), 1983 (1971).

12D. Kojima, S., Ogawa, S., Minematsu, M., and Tanaka, M., Effects of impurities on nuclear quadrupole resonance in *p*-dichlorobenzene, *J. Phys. Soc. Jap.*, 13(5), 446 (1955).

13D. Schultz, H. and Karr, C., Jr., Quantitative aspects of NQR spectroscopy of inorganics and minerals, *Anal. Chem.*, 41(4), 661 (1969).

14D. Moross, G. G. and Story, H. S., Temperature dependence of the nuclear quadrupole resonance frequencies in *p*-dichlorobenzene, *J. Chem. Phys.*, 45(9), 3370 (1966).
15D. Tokuhiro, T., Temperature dependence of the nuclear quadrupole relaxation time T_1 in *p*-dichlorobenzene under constant pressure, *J. Chem. Phys.*, 41(4), 1147 (1964).
16D. Partlow, W. D. and Moulton, W. G., Temperature dependence of the ^{35}Cl pure quadrupole resonance in $NaClO_3$, *J. Chem. Phys.*, 39, 2381 (1963).
17D. Barton, B. L., Temperature dependence of the nuclear quadrupole resonant frequency of ^{35}Cl in 3-chloro-1-propyne, *J. Chem. Phys.*, 51, 5726 (1969).
18D. Vijaya, M. S. and Ramakrishna, J., Temperature dependence of chlorine nuclear quadrupole resonances in 1,3,5-trichlorobenzene and 1-chloro-2,4-dinitrobenzene, *Mol. Phys.*, 19(1), 131 (1970).
19D. Bayer, H., Zur Theorie der Spin-Gitter-Relaxation in Molekülkristallen, *Z. Phys.*, 130, 227 (1951).
20D. Hass, T. E. and Marram, E. P., Temperature dependence of chlorine NQR frequencies and pi bonding, *J. Chem. Phys.*, 43, 3985 (1965).

Articles on Interpretation of Nitrogen-containing Spectra

1E. Casabella, P. A. and Bray, P. J., ^{14}N quadrupole interaction with an asymmetric field gradient, *J. Chem. Phys.*, 29(5), 1105 (1958).
2E. Negita, H. and Bray, P. J., ^{14}N pure quadrupole resonances of several nitriles, *J. Chem. Phys.*, 33(6), 1876 (1960).
3E. Negita, H., Casabella, P. A., and Bray, P. J., ^{14}N pure quadrupole resonances of acetonitrile and hydrocyanic acid, *J. Chem. Phys.*, 32(1), 314 (1960).
4E. Guibe, L., Etude De Nouvelles Resonances Quadripolaires Pures Des Noyaux D'Azote, *Ann. Phys.* (Paris), 7, 177 (1962).
5E. Lehrer, S. S. and O'Konski, C. T., Nuclear quadrupole resonance and bonding in crystalline ammonia, *J. Chem. Phys.*, 43, 1941 (1965).
6E. Matzkanin, G. A., Scott, T. A., and Haigh, P. J., Nuclear resonance in solid nitrogen trifluoride, *J. Chem. Phys.*, 42(5), 1646 (1965).
7E. Alexander, S. and Tzalmona, A., Relaxation by slow motional processes. Effect of molecular rotations in pure quadrupole resonance, *Phys. Rev.*, 138(3A), A845 (1965).
8E. O'Konski, C. T. and Torizuka, K., Spin-lattice relaxation and saturation of ^{14}N quadrupole resonance in urea, *J. Chem. Phys.*, 51, 1, 461 (1969).
9E. Tzalmona, A., Measurements of ^{14}N quadrupole interaction and motional processes in piperazine, *Phys. Lett.*, 20(5), 478 (1966).
10E. Ikeda, R., Nakamura, D., and Kubo, M., Pure quadrupole resonance of nitrogen-14 in some organic thiocyanates, *J. Phys. Chem.*, 70(11), 3626 (1966).
11E. Abe, Y., Kamishima, Y., and Kojima, S., Nuclear quadrupole coupling constants of ^{14}N of hydrazine, *J. Phys. Soc. Jap.*, 21, 2083 (1966).
12E. Schempp, E. and Bray, P. J., Nuclear quadrupole resonance in solid diazines, *J. Chem. Phys.*, 46(3), 1186 (1967).
13E. Singh, K. and Singh, S., ^{14}N quadrupole resonance in benzene sulphonamide, *Indian J. Phys.*, 41, 862 (1967).
14E. Schempp, E. and Bray, P. J., Nuclear quadrupole resonance in crystalline pyrrole, *J. Chem. Phys.*, 48, 2380 (1968).
15E. Zussman, A. and Alexander, S., Pure nuclear quadrupole resonance in triethylene diamine, *J. Chem. Phys.*, 48(5), 3534 (1968).
16E. Ikeda, R., Onda, S., Nakamura, D., and Kubo, M., Nuclear quadrupole resonance of nitrogen-14 in some pyridine derivatives, *J. Phys. Chem.*, 72(7), 2501 (1968).
17E. Ikeda, R., Nakamura, D., and Kubo, M., Pure quadrupole resonance of nitrogen-14 in some metal complexes, *J. Phys. Chem.*, 72(8), 2982 (1968).
18E. Haigh, P. J., Canepa, P. C., Matzkanin, G. A., and Scott, T. A., Nuclear resonances in the solid methylamines. I*, *J. Chem. Phys.*, 48(9), 4234 (1968).
19E. Oja, T., Marino, R. A., and Bray, P. J., The temperature dependence of ^{14}N nuclear quadrupole resonance in barium nitrite, *Phys. Lett.*, 28A(1), 16 (1968).
20E. Schempp, E. and Bray, P. J., ^{14}N nuclear quadrupole resonance in substituted pyridines, *J. Chem. Phys.*, 49(8), 3450 (1968).
21E. Osokin, D. Ya., Safin, I. A., and Nuretdinov, I. A., ^{14}N nuclear quadrupole resonance in some amines, *Dokl. Phys. Chem. (SSSR)*, 186, 393 (1969).
22E. Betsuyaku, H., Calculation of the ^{14}N quadrupole coupling constant in the nitrite ion, *J. Chem. Phys.*, 50, 3117 (1969).
23E. Colligiani, A., Ambrosetti, R., and Angelone, R., New nuclear quadrupole resonance frequencies at ^{14}N in saturated cyclic amines, *J. Chem. Phys.*, 52(4), 2005 (1970).
24E. Osokin, D. Ya., Safin, I. N., and Nuretdinov, I. A., Nuclear quadrupole resonance in some three-membered nitrogen heterocycles, *Dokl. Chem.*, 190, 54 (1970).
25E. Ha, T. K. and O'Konski, E. T., Nuclear quadrupole resonance of ^{14}N in ethylenimine, *Z. Naturforsch.*, Band 25a, Heft 7, 1970.

26E. Colligiani, A., Ambrosetti, R., and Guibe, L., Nuclear quadrupole resonance of ^{14}N of the –CN group in some *para*-substituted benzonitriles, *J. Chem. Phys.*, 54(5), 2105 (1971).
27E. Tzalmona, A., Nuclear quadrupole resonance and relaxation of ^{14}N in CH_3CN, *Phys. Lett.*, 34A(5), 289 (1971).
28E. Eletr, S. and O'Konski, C. T., ^{14}N nuclear quadrupole resonance study of hydrogen bonding in $NH_3 \cdot 1/2\, H_2O$, *J. Chem. Phys.*, 54(10), 4312 (1971).
29E. Onda, S., Harada, H., Nakamura, D., and Kubo, M., NQR of nitrogen-14 in some primary aliphatic amines, *J. Mag. Res.*, 8, 238 (1972).

UNREVIEWED REFERENCES

Articles on Interpretation of Chlorine-containing Spectra

1. Adrian, F. J., Electric field gradient asymmetry in solid chlorine, *J. Chem. Phys.*, 38, 1258 (1963).
2. Agranat, I., Gill, D., Hayek, M., and Loewenstein, R. M. J., NQR spectrum and the spatial structure of octachloropentafulvalene. Noncovalent intramolecular interactions of bucking C–Cl groups, *J. Chem. Phys.*, 51, 2756 (1969).
3. Arbuzov, B. A., Vulf'son, S. G., Safin, I. A., Biryukov, I. P., and Vereshchagin, A. N., Inductive interaction of the C–Cl bonds and nuclear quadrupole resonance spectra of Cl^{35} in chlorosubstituted ethanoanthracenes, *Bull. Acad. Sci. SSSR, Div. Chem. Sci.*, 1178 (1970).
4. Babushkina, T. A., Baisa, D. F., and Robas, V. I., NQR of ^{35}Cl in the α-phase of *m*-dichlorobenzene, *J. Struct. Chem.*, 5(1), 119 (1964).
5. Babushkina, T. A., Robas, V. I., and Semin, G. K., NQR in polymers, *Dokl. Akad. Nauk SSSR*, 159, 164 (1964).
6. Babushkina, T. A. and Semin, G. K., Study of the peculiarities of phase transitions in dihalogen-substituted methanes by NQR, *Zh. Strukt. Khim.*, 7(1), 114 (1966).
7. Bartenev, G. M. and Luk'yanov, I. A., Use of radispectroscopic methods for investigating polymers, *Soviet Plastics*, No. 12, 46 (1964).
8. Barton, B. L., Pure nuclear quadrupole resonance of ^{35}Cl in 1,4-dichloro-2-butyne, *J. Chem. Phys.*, 51(10), 4670 (1969).
9. Barton, B. L., Pure nuclear quadrupole resonance of ^{35}Cl in 1,1,1-trichloro-2,2,2-trifluoroethane, *J. Chem. Phys.*, 51, 4672 (1969).
10. Barton, B. L., Temperature dependence of the nuclear quadrupole resonance and lattice frequencies of methyl chloride, *J. Chem. Phys.*, 54, 814 (1971).
11. Bennett, R. A. and Hooper, H. O., ^{35}Cl nuclear quadrupole resonance from some charge-transfer complexes, *J. Chem. Phys.*, 47, 4855 (1967).
12. Bersohn, R. and Shulman, R. G., Measures of covalency in transition-metal chlorides, *J. Chem. Phys.*, 45(6), 2298 (1966).
13. Bishop, J. K. B., Cullen, W. R., and Gerry, M. C. L., ^{35}Cl NQR of some phosphorus-chlorine compounds, *Can. J. Chem.*, 49, 3910 (1971).
14. Bray, P. J. and Ring, P. J., Chlorine quadrupole resonances in solids, *J. Chem. Phys.*, 21, 2226 (1953).
15. Bray, P. J. and Esteva, D., Cl in SO_2Cl pure quadrupole spectra, *J. Chem. Phys.*, 22, 570 (1954).
16. Bray, P. J., Barnes, R. G., and Bersohn, R., Pure quadrupole resonances in multichlorobenzenes, *J. Chem. Phys.*, 25(5), 813 (1956).
17. Brill, T. B. and Hugus, Z. Z., Jr., Interpretations of nuclear quadrupole resonance data in some *trans*-dichlorobis-(ethylenediamine) cobalt (III) salts, *J. Phys. Chem.*, 74(15), 3022 (1970).
18. Bronswyk, W. van and Nyholm, R., Chlorine nuclear quadrupole coupling in platinum and palladium dichlorides, *J. Chem. Soc. (A)*, Inorg. Phys.-Theoret., 2084 (1968).
19. Bucci, P., Cecchi, P., and Colligiani, A., Zeeman effect of the nuclear quadrupole resonance of chlorine-35 in 3,5 and 2,6-dichloropyridine, *J. Am. Chem. Soc.*, 87(13), 3027 (1965).
20. Bucci, P., Cecchi, P., and Colligiani, A., Zeeman effect of the nuclear quadrupole resonance of ^{81}Br in *para*-bromophenol and ^{35}Cl in *para*-chlorophenol, *J. Chem. Phys.*, 50(1), 530 (1969).
21. Budak, H., Pure quadrupole resonance frequency shift and internal stress in gamma-ray irradiated sodium chlorate, *Nature*, 208, 382 (1965).
22. Carlson, E. H. and Adams, H. S., Chlorine nuclear quadrupole resonance in ER Cl_3 and some similar chlorides, *J. Chem. Phys.*, 51(1), 388 (1969).
23. Carr, S. L., Garrett, B. B., and Moulton, W. G., Nuclear quadrupole resonance of $(NH_4)_2\ (InCl_5H_2O)$, *J. Chem. Phys.*, 47(3), 1170 (1967).
24. Chihara, H., Nakamura, N., and Irie, T., Nuclear quadrupole resonance in *syn*- and *anti*-7-chloronorbornene, *Bull. Chem. Soc. Jap.*, 42, 3034 (1969).
25. Cohen, A. J. and Whitehead, M. A., CNDO/BW calculations of the ^{35}Cl NQR frequency in –NCl, COCl, –OCOCl molecules, *Trans. Faraday Soc.*, II, No. 4, 649 (1972).
26. Cotton, F. A. and Harris, C. B., Correlation of nuclear quadrupole coupling constants with molecular electronic structure using molecular orbital theory, *Proc. Natl. Acad. Sci. USA*, 56, 12 (1966).

27. Dean, C., Chlorine nuclear quadrupole resonances in solid solutions, *J. Chem. Phys.*, 23, 1734 (1955).

28. Dewar, M. J. S. and Lucken, E. A. C., Chemical applications of nuclear quadrupole resonance spectroscopy. Part I. Some chloro-derivatives of nitrogen heterocycles, *J. Chem. Soc.*, 2653 (1958).

29. Dewar, M. J. S. and Lucken, E. A. C., Chemical applications of nuclear quadrupole resonance spectroscopy. Part II. Chloro-derivatives of maleic anhydrides, thiophene, and anilinium salts, *J. Chem. Soc.*, 426 (1959).

30. Dewar, M. J. S. and Herr, M. L., Chlorine NQR spectra of some benzyl chlorides, alkyl chlorides, and chlorophosphines, *Tetrahedron*, 27, 2377 (1971).

31. Dewar, M. J. S., Herr, M. L., and Marchand, A. P., Chlorine NQR spectra of chloronorbornanes and chloronorbornenes, *Tetrahedron*, 27, 2731 (1971).

32. DiLorenzo, J. V. and Schneider, R. F., Chlorine nuclear quadrupole resonance in $(C_2H_5)_4$-$NAsCl_6$, *J. Phys. Chem.*, 72(2), 761 (1968).

33. Dinesh and Narasimhan, P. T., Zeeman study of the ^{35}Cl NQR spectrum of chlorobenzene, *J. Chem. Phys.*, 49(6), 2519 (1968).

34. Dixon, M., Jenkins, H. D. B., Smith, J. A. S., and Tong, D. A., Nuclear quadrupole resonance of ^{35}Cl in phosphonitrilic chloride tetramer, *Trans. Faraday Soc.*, 63, Pt. 12, 2852 (1967).

35. Dreyfus, B., Contribution a l'etude des imperfections dans les solides par la resonance quadrupolaire nucléaire, *Ann. Phys.*, 3, 683 (1958).

36. Evans, J. C. and Lo, G. Y-S, Chlorine nuclear quadrupole resonance in the hydrogen dichloride ion, *J. Phys. Chem.*, 70(8), 2702 (1966).

37. Evans, J. C. and Lo, G. Y-S, Chlorine nuclear quadrupole coupling in iodobenzene dichloride, *J. Phys. Chem.*, 71(8), 2730 (1967).

38. Evans, J. C. and Lo, G. Y-S, Chlorine nuclear quadrupole resonance in the symmetrical hydrogen dichloride ion, *J. Phys. Chem.*, 71(11), 3697 (1967).

39. Evans, J. C. and Lo, G. Y-S, Chlorine nuclear quadrupole coupling in iodine trichloride and in its adduct with aluminum trichloride, *Inorg. Chem.*, 6(4), 836 (1967).

40. Fedin, E. I. and Kitaigorodskii, A. I., Nuclear quadrupole resonance studies of solid solutions of some organic compounds, *Soviet Physics–Crystallography*, 6(3), 322 (1961).

41. Fergusson, J. E. and Scaife, D. E., Temperature dependence of chlorine NQR frequency in second row transition hexachlorometallates, *Inorg. Nucl. Chem. Lett.*, 7, 987 (1971).

42. Frausto Da Silva, J. J. R. and Wootton, R., Nuclear quadrupole resonance spectra of pyridine *N*-oxide complexes of copper (II) halides, *Chem. Commun.*, 403 (1970).

43. Graybeal, J. D. and Green, P. J., Nuclear quadrupole resonance Zeeman study of polycrystalline group IVa tetrachlorides, *J. Phys. Chem.*, 73(9), 2948 (1969).

44. Graybeal, J. D., McKown, R. J., and Ing, S. D., Pure nuclear quadrupole resonance in hexachlorostannates of hydrated divalent cations, *J. Phys. Chem.*, 74(8), 1814 (1970).

45. Grechishkin, V. S. and Kyuntsel, I. A., NQR in some crystalline charge-transfer complexes, *Zh. Strukt. Khim.*, 7(1), 119 (1966).

46. Grechishkin, V. S., Gordeev, A. D., and Ainbinder, N. E., Quandrupole relaxation in Menshutkin complexes at low temperatures, *Zh. Strukt. Khim.*, 7(3), 465, (1966).

47. Green, P. J. and Graybeal, J. D., Nuclear quadrupole coupling in organotin chlorides. II. Dichlorides, *J. Am. Chem. Soc.*, 89(17), 4305 (1967).

48. Haas, T. E. and Welsh, S. M., Chlorine-35 nuclear quadrupole resonance and the structure of the bichloride ion in tetramethylammonium bichloride, *J. Phys. Chem.*, 71(10), 3363 (1967).

49. Hammel, J. C., Lynch, R. J., Smith, J. A. S., Barabasi, and Isfan, E., Electric field effects in magnetic resonance. Part II. ^{35}Cl quadrupole resonance frequencies, *J. Chem. Soc. (A)*, 3000 (1969).

50. Hart, R. M. and Whitehead, M. A., ^{35}Cl NQR of the N–Cl bond, *Trans. Faraday Soc.*, 67, 1569 (1971).

51. Hart, R. M. and Whitehead, M. A., ^{35}Cl NQR of fifty-nine molecules containing the S–Cl bond, *Trans. Faraday Soc.*, 67, 3451 (1971).

52. Hart, R. M. and Whitehead, M. A., Chlorine NQR of phosphorus-chlorine compounds, *J. Chem. Soc. (A)*, 1738 (1971).

53. Hayek, M., Gill, D., Agranat, I., and Rabinovitz, M., NQR of ^{35}Cl in two solid phases of hexachlorocyclopentadiene, *J. Chem. Phys.*, 47, 3680 (1967).

54. Holmes, R. R., Carter, R. P., Jr., and Peterson, G. E., Molecular structures of PCl_4F, PCl_3F_2, and PCl_2F_3, *J. Inorg. Chem.*, 3, 1748 (1964).

55. Holmes, R. R. and Carter, R. P., Jr., Pentacoordinated molecules. VI. The electric-dipole moment of PCl_3F_2 and PCl_2F_3 in the gaseous state, *J. Chem. Phys.*, 43(5), 1645 (1965).

56. Hooper, H. O. and Bray, P. J., Induction studies in several groups of halogen containing organic compounds by their ^{35}Cl, ^{79}Br, or ^{81}Br pure quadrupole resonance spectra, *J. Chem. Phys.*, 33(2), 334 (1960).

57. Hughes, W. E., Montgomery, C. G., Moulton, W. G., and Carlson, E. H., Nuclear quadrupole resonance in paramagnetic $PrCl_3$, *J. Chem. Phys.*, 41(11), 3470 (1964).

58. Kaplansky, M., Clipsham, R., and Whitehead, M. A., Chlorine-35 nuclear quadrupole resonance in inorganic molecules containing phosphorus and sulphur, *J. Chem. Soc. (A)*, 584 (1969).

59. Kozima, K. and Saito, S., Nuclear quadrupole resonance of dichlorocyclohexanone, *J. Chem. Phys.*, 31, 560 (1959).
60. Vignaneswara, Kumar U. and Rao, B. D. N., Chlorine-35 quadrupole resonance in $Ca(ClO_3)_2 \cdot 2H_2O$, *Phys. Status Solidi (B)*, 44, 203 (1971).
61. Linscheid, P. and Lucken, E. A. C., The effects of confirmation on nuclear quadrupole coupling constants of α-chloro ethers, *Chem. Commun.*, 425 (1970).
62. Livingston, R., Pure quadrupole spectra: aliphatic chlorine compounds, *J. Chem. Phys.*, 20(7), 1170 (1952).
63. Livingston, R., Pure quadrupole spectra of solid chlorine compounds, *J. Phys. Chem.*, 57, 496 (1953).
64. Lucken, E. A. C. and Whitehead, M. A., Chemical applications of nuclear quadrupole resonance. Part IV. The transmission of the electronic effect of various substituents by a phosphorus atom, *J. Chem. Soc.*, 2459 (1961).
65. Lucken, E. A. C. and Mazeline, C., Chemical applications of nuclear quadrupole resonance spectroscopy. Part V. The trichlorocyclopropenium ion, *J. Chem. Soc. (A)*, 153 (1968).
66. Marram, E. P. and Ragle, J. L., Pure quadrupole resonance in 1,2-dichloroethane-*d*, *J. Chem. Phys.*, 37, 3015 (1962).
67. Michel, R. E. and Spence, R. D., Effect of impurities on the ^{35}Cl quadrupole resonance in C_6H_5Cl, *J. Chem. Phys.*, 26(4), 954 (1957).
68. Monfils, A. and Grosjean, D., Intensité de Spectres Nucléaires Quadripolaires des Solutions Solides, *Physica*, XXII, 541 (1956).
69. Morino, Y., Miyagawa, I., Chiba, T., and Shimozawa, T., Pure quadrupole spectra of the isomers of benzene hexachloride, *J. Chem. Phys.*, 25, 185 (1956).
70. Morosin, B. and Narath, A., X-ray diffraction and NQR studies of chromium trichloride, *J. Chem. Phys.*, 40(7), 1958 (1964).
71. Musher, J. I., Effects of intramolecular electric fields in molecules: EQR coupling constants, *J. Chem. Phys.*, 37(10), 2372 (1962).
72. Myasnikov, R. M., Robas, W. I., and Semin, G. K., Notes on the structure of β-chloronaphthalene crystals, *Zh. Strukt. Khim.*, 6(3), 474 (1965).
73. Nakamura, D., Kurita, Y., Ito, K., and Kubo, M., Covalency of metal-ligand bonds in potassium hexahaloplatinates (IV) studied by the pure quadrupole resonance of halogens, *J. Am. Chem. Soc.*, 82, 5783 (1960).
74. Nakamura, D., Ito, K., and Kubo, M., Covalency of metal-ligand bonds in hexahalotellurates (IV) studied by the pure quadrupole resonance of halogens, *J. Am. Chem. Soc.*, 84, 163 (1962).
75. Peneau, A., Guibe, L., and Kastler, A., Studies of the 2,4,6-trichloroanizole by pure chlorine quadrupole resonance, *C.R. Acad. Sci.* (Paris), Ser. B 1321 (1968).
76. Peterson, G. E. and Bridenbaugh, P. M., Nuclear quadrupole resonance Zeeman study of *para*-chlorophenol, *J. Chem. Phys.*, 46(7), 2644 (1967).
77. Peterson, G. E., Steed, N., and Bridenbaugh, P. M., Nuclear quadrupole resonance Zeeman study of 2,4-dichlorophenoxyacetic acid, *J. Chem. Phys.*, 47(7), 2262 (1967).
78. Peterson, G. E. and Bridenbaugh, P. M., NQR Zeeman study of gallium trichloride, *J. Chem. Phys.*, 51(1), 238 (1969).
79. Pies, W. and Weiss, A., Studies of the substituent effect in aromatic systems by chlorine NQR (^{35}Cl-NQR). Chloroanilinium salts, *Z. Naturforsch. B*, 26, 555 (1971).
80. Ragle, J. L. and Sherk, K. L., Deuteron quadrupole coupling in some solid chlorinated hydrocarbons, *J. Chem. Phys.*, 50(8), 3553 (1969).
81. Rehn, V., Covalent-bond asymmetries from Zeeman-split NQR, *J. Chem. Phys.*, 38(3), 749 (1963).
82. Richardson, C. B., Temperature dependence of the Zeeman effect in the nuclear quadrupole resonance in chloranil, *J. Chem. Phys.*, 38(2), 510 (1963).
83. Rogers, M. T. and Ryan, J. A., Chlorine nuclear quadrupole resonance study of some molecular adducts of phosphorus oxychloride, *J. Phys. Chem.*, 72(4), 1340 (1968).
84. Roll, D. B. and Biros, F. J., Nuclear quadrupole resonance spectrometry of some chlorinated pesticides, *Anal. Chem.*, 41, 407 (1969).
85. Saito, Y., ^{35}Cl and ^{37}Cl magnetic resonance of simple chlorine compounds, *Can. J. Chem.*, 43, 2530 (1965).
86. Sasikala, D. and Murty, C. R. K., NQR Zeeman spectra of chlorine in 3,4-dichloronitrobenzene, *J. Phys. Chem., Solid State Phys.*, 4, 3322 (1971).
87. Schneider, R. F. and DiLorenzo, J. V., Chlorine and antimony nuclear quadrupole resonance in $SbCl_5$, CH_3CN, $SbCl_5POCl_3$, and $SbCl_5$, *J. Chem. Phys.*, 47(7), 2343 (1967).
88. Schreiner, A. F. and Brill, T. B., A comparative characterization of the metal-chlorine bonds in *trans*-$(Men_2Cl_2)^+$ ions (M = Rh, Co, Cr) using ^{35}Cl NQR spectroscopy, *Inorg. Nucl. Chem. Lett.*, 6, 355 (1970).
89. Semin, G. K., Induction transmission of influence along a carbon chain in nuclear quadrupole resonance spectra (empirical scheme for calculating the NQR frequencies of ^{35}Cl in aliphatic molecules), *Dokl. Phys. Chem. (SSSR)*, 158, 951 (1964).
90. Semin, G. K., Nuclear quadrupole resonance of ^{35}Cl and ^{79}Br in polychloro- and polybromoethanes, *Zh. Strukt. Khim.*, 6(6), 916 (1965).
91. Singh, K. and Singh, S., NQR in hexachloro-ethane, *J. Phys. Soc. Jap.*, 32(1), 210 (1971).

92. Smith, P. W. and Stoessiger, R., Cation effects in nuclear quadrupole resonance spectroscopy, *Mol. Phys.*, 17(5), 503 (1969).
93. Smith, J. A. S. and Tong, D. A., NQR studies of boron-chlorine compounds. Part II. Chlorine-35 quadrupole resonance frequencies, *J. Chem. Soc. (A)*, 178 (1971).
94. Stidham, H. D. and Farrell, H. H., Chlorine-35 nuclear quadrupole resonance spectra of several chlorodiazines, *J. Chem. Phys.*, 49, 2463 (1968).
95. Strehlow, W. H., ^{35}Cl NQR of 1,2-dichloronaphthalene, *J. Chem. Phys.*, 55(5), 2607 (1971).
96. Swiger, E. D. and Graybeal, J. D., Nuclear quadrupole coupling in organotin halides. I. Phenyl- and n-butyltin chlorides, *J. Am. Chem. Soc.*, 87(7), 1464 (1965).
97. Todd, J. E., Whitehead, M. A., and Weber, K. E., Pure nuclear quadrupole resonances of several chlorinated cyclopropanes, *J. Chem. Phys.*, 39(2), 404 (1963).
98. Tokuhiro, T., Effect of hindered rotation on the NQR frequency and the linewidth in trans-1,2-dichloroethane, *J. Chem. Phys.*, 41(2), 438 (1964).
99. Tokuhiro, T., Effects of molecular motion on the nuclear quadrupole resonance frequencies and linewidths in some solid alkyl halides, *J. Chem. Phys.*, 47(7), 2353 (1967).
100. Tovborg-Jenson, N., NQR investigation of phase transitions in cesium plumbochloride, *J. Chem. Phys.*, 50, 559 (1969).
101. Tsvetkov, E. N., Semin, G. K., Lobanov, D. I., and Kabachnik, M. I., Correlation of the nuclear quadrupole resonance frequencies of ^{35}Cl monosubstituted chlorobenzenes with δ-Hammett constants, *Tetrahedron Lett.*, 26, 2521 (1967).
102. Vijaya, M. S. and Ramakrishna, J., Temperature dependence of nuclear quadrupole resonance in 1,2-dichloro-3-nitrobenzene, *J. Chem. Phys.*, 53, 4714 (1970).
103. Weber, M. J. and Hahn, E. L., Selective spin excitation and relaxation in nuclear quadrupole resonance, *Phys. Rev.*, 120(2), 365 (1960).
104. Woessner, D. E. and Gutowsky, H. S., ^{35}Cl pure quadrupole resonance studies of relaxation times in solid solutions of p-dichlorobenzene, *J. Chem. Phys.*, 27(5), 1072 (1957).
105. Woessner, D. E. and Gutowsky, H. S., Nuclear pure quadrupole relaxation and its temperature dependence in solids, *J. Chem. Phys.*, 39(2), 440 (1963).
106. Zeil, W. and Haas, B., Kernquadrupolresonanzspektroskopishche Untersuchungen an Choloracetylenen des Typs $(CH_3)_3$–X–C=C–Cl(X=C, Si, Ge, Sn), *Z. Naturforsch.*, 229, 2011 (1967).
107. Zeil, W. and Haas, B., Das Kernquadrupolresonanzspektrum des Oktachlorpropans ($CCl_3CCl_2CCl_3$), *Z. Naturforsch.*, 23A, 1225 (1968).

Articles on Interpretation of Nitrogen-containing Spectra

1. Alexander, S. and Tzalmona, A., Measurement of molecular rotation by ^{14}N nuclear quadrupole resonance relaxation times, *Phys. Rev. Lett.*, 13(18), 546 (1964).
2. Barton, B. L., Rotational vibrations of pyrazine from temperature dependent ^{14}N nuclear quadrupole resonance and x-ray thermal tensors, *J. Chem. Phys.*, 55(4), 1984 (1971).
3. Boguslavskii, A. A. and Semin, G. K., Effect of external electric field on nuclear quadrupole resonance spectra, *Soviet Physics–Solid State*, 11(12), 3034 (1970).
4. Colligiani, A., Guibe, L., Haigh, P. J., and Lucken, E. A. C., The ^{14}N nuclear quadrupole constants of organic nitriles, *Mol. Phys.*, 14(1), 89 (1968).
5. Edmonds, D. T. and Speight, P. A., Nitrogen quadrupole resonance in amino acids, *Phys. Lett.*, 34A(6), 325 (1971).
6. Eletr, S., Nuclear quadrupole resonance in hexamethylene-tetramine: modulation and reorientational broadening, *J. Chem. Phys.*, 53(2), 543 (1970).
7. Forman, R. A., Nuclear magnetic resonance of nitrogen-14 in potassium azide, *J. Chem. Phys.*, 45(4), 1118 (1966).
8. Ha, T. K. and O'Konski, C. T., Nuclear quadrupole resonance of ^{14}N in pyridine complexes, *Z. Naturforsch.*, Band 25, Heft 10 (1970).
9. Haigh, P. J. and Scott, T. A., Effects of ^{15}N on the nuclear quadrupole resonance of ^{14}N in solid N_2, *J. Chem. Phys.*, 38(1), 117 (1963).
10. Hartland, A., A pulsed double resonance study of the nuclear quadrupole interactions of ^{14}N in $NH_4H_2PO_4$, *J. Phys. Chem.*, Ser 2, 2, 264 (1969).
11. Kadaba, P. K., O'Reilly, D. E., and Blinc, R., ^{14}N nuclear quadrupole resonance in ferroelectric $NaNO_2$, *Phys. Status Solidi*, 42, 855 (1970).
12. Kamishina, Y., Zeeman study of nuclear quadrupole resonance of nitrogen in hydrazine, *J. Phys. Soc. Jap.*, 31(1), 242 (1971).
13. Krause, L. and Whitehead, M. A., ^{14}N nuclear quadrupole resonance frequencies of several nitrogen containing compounds, *J. Chem. Phys.*, 52, 2787 (1970).
14. Krause, L. and Whitehead, M. A., Nitrogen-14 nuclear quadrupole resonance of substituted anilines, *J. Chem. Soc.*, 12, 2433 (1971).
15. Marino, R. A., Guibe, L., and Bray, P. J., ^{14}N nuclear quadrupole resonance in aminopyridines, *J. Chem. Phys.*, 49(11), 5104 (1968).

16. Matzkanin, G. A., O'Neal, T. N., and Scott, T. A., Temperature and pressure dependence of the nuclear quadrupole resonance of ^{14}N in $(CH_2)_6N_4$, *J. Chem. Phys.*, 44(11), 4171 (1966).
17. Negita, H., Line shape of ^{14}N pure quadrupole resonance by the Zeeman modulation, *J. Chem. Phys.*, 44(5), 1734 (1966).
18. Negita, H., Hayashi, M., Hirakawa, T., and Kuwata, H., ^{14}N nuclear quadrupole resonances of 2,2′ and 4,4′-dipyridyls, *Bull. Chem. Soc. Jap.*, 43, 2262 (1970).
19. O'Konski, C. T. and Ha, T. K., Interpretation of nuclear coupling in nitrogen containing molecules with *ab initio* molecular-orbital wavefunctions, *J. Chem. Phys.*, 49(12), 5354 (1968).
20. Osokin, D. Ya. and Safin, I. A., Study of hindered rotations of separate groups of atoms in some amines by nuclear quadrupole resonance of ^{14}N, *Soviet Physics–Solid State*, 11(12), 3025 (1970).
21. Schempp, E. and Bray, P. J., Nuclear quadrupole resonance data as a sensitive check on calculated molecular wavefunctions, *J. Chem. Phys.*, 48, 2381 (1968).
22. Schempp, E., ^{14}N and ^{35}Cl nuclear quadrupole resonance in nitrogen-chlorine bonds, *Chem. Phys. Lett.*, 8(6), 562 (1971).
23. Tzalmona, A., Anisotropy of molecular rotations measured by NQR relaxation, *J. Chem. Phys.*, 50, 366 (1969).
24. Widman, R. H., Shifts of the nuclear quadrupole resonance spectra of ^{14}N in urea, cyanuric acid, and melamine, *J. Chem. Phys.*, 43, 2922 (1965).