

# High Sensitivity Nuclear Quadrupole Resonance of Light Nuclei

Donald T. Edmonds

Clarendon Laboratory of Physics  
Oxford University  
Oxford, England

## I. WHAT IS NQR?

Nuclear quadrupole resonance (NQR) is the study of the energy splittings due to interaction of the electric quadrupole moment of the nucleus with the electric field gradient that exists at the nuclear site. Many nuclei with spins greater than  $\frac{1}{2}$  have a quadrupole moment and most of these quadrupole moments have been measured and tabulated. Thus, the information gained by studying NQR is the magnitude, orientation, and symmetry of the electric field gradient at the nuclear site. In general, the electric field gradient may be expressed in a set of axes ( $oxyz$ ) as a collection of nine second derivatives of the electrostatic potential  $V$ , such as  $V_{xx} = \partial^2 V / \partial x^2$ ,  $V_{xy} = \partial^2 V / \partial x \partial y$  etc. As with moments of inertia, it is possible, by choosing a particular set of axes ( $OXYZ$ ), called the principal axes, to reduce these nine parameters to three, namely  $V_{xx}$ ,  $V_{yy}$ , and  $V_{zz}$ . Even these three parameters are not independent as, in a region of no charge, the Laplace equation  $\Delta V = 0$  demands that

$$V_{xx} + V_{yy} + V_{zz} = 0$$

Thus, an electric field gradient is entirely determined if its principal axes are known and if two

parameters derived from  $V_{xx}$ ,  $V_{yy}$ , and  $V_{zz}$  are given. The two chosen are  $V_{zz}$ , which characterizes the maximum electric field gradient, and  $\eta = (V_{yy} - V_{xx}) / V_{zz}$ , the anisotropy constant which describes the symmetry of the electric field gradient about the  $OZ$  axis.  $\eta$  is a dimensionless number between 0 and 1.

By measuring two resonance lines in the NQR spectrum of a powder, both  $V_{zz}$  and  $\eta$  are obtained with no ambiguity. With a single crystal, the directions of the principal axes of the electric field gradient are obtainable by measuring the NQR spectrum in the presence of a small applied magnetic field. Even in a powder sample the fine structure of the NQR lines may reveal information of the directions of the principal axes relative to neighbouring nuclei such as nearby protons.

## II. WHY MEASURE NQR SPECTRA?

The electric field gradient in a solid may be thought of as arising from either intramolecular or intermolecular charge distributions. The intramolecular component is in fact an average of  $(3Z^2 - R^2) / R^5$  taken over the electronic wavefunctions of the molecule together with a contribution from the

other positively charged nuclei in the molecule. For most non-ionic solids, the intramolecular contribution dominates so that NQR provides a rather direct measure of the electronic structure of the molecule. Moreover, the electronic structure may be measured at many sites within the molecule where a nucleus with a quadrupole moment is situated. The calculation of the electric field gradient at the nucleus of a heavy atom is complicated by shielding effects which are caused by the distortion of inner electron orbits in response to the electric fields generated by outer electron orbits. For lighter elements, these shielding effects are much smaller and the calculation of the electric field gradient should be a rather sensitive test of the accuracy of the wavefunctions used to represent the electronic structure of the molecule. In fact, not many such calculations have been performed to date, partly because, until very recently, the NQR spectra of light elements were impossible to measure. The experimental situation has improved recently, as we shall see, so that much more theoretical work in this area can be expected.

The intermolecular contribution to the electric field gradient also yields valuable information. It can be used, for example, to sense changes in the structure of solids due to phase changes. It has also proved to be an extremely sensitive measure of changes in hydrogen bonding between molecules. For example, a change in an O-H bond length of only 0.05 Å due to changes in hydrogen bonding can cause the frequency of the NQR of a deuteron substituted for the proton to shift from around 100 kHz to around 200 kHz. As the deuteron spectral lines are now routinely measured to  $\pm 0.1$  kHz, the sensitivity of deuteron NQR to hydrogen bonding is higher than that of any other technique used to date.

In addition to the intermolecular contribution to the electric field gradient, intermolecular and intramolecular magnetic dipole coupling can cause the measured NQR lines to display multiplet structure which yields valuable structural information about the solid employed. In NMR, most of the information obtained is from fine structure and from small frequency shifts due to spin-spin coupling and chemical shifts. Unlike in NMR, in NQR the unshifted spectral line contains valuable structural information but additional information is obtained from fine structure of the NQR lines.

The most important advantage of NQR over NMR or even X-ray and neutron diffraction is that high

resolution spectra are obtainable in powdered solids or frozen liquids. It is a truly microscopic technique and does not require long range order to exist. As the experiment is performed in zero applied steady magnetic field, no special direction is imposed upon the specimen from outside. Provided that the local environment of a nucleus is the same in many molecules, narrow NQR spectral lines are obtained irrespective of the orientation of one molecule relative to another.

### III. WHAT ARE THE SPECIAL ADVANTAGES OF MEASURING NQR FOR LIGHT NUCLEI?

Light nuclei have simple electronic structures which hold out the promise of rapid advances in the theoretical understanding of electric field gradients and in their calculation from known wavefunctions. We have already mentioned the much reduced shielding effects in light nuclei. Another importance of light nuclei is that elements such as  $^2\text{D}$  (substituted for  $^1\text{H}$ ),  $^{14}\text{N}$ ,  $^{17}\text{O}$ , and  $^{23}\text{Na}$  often play an important role in the binding and function of chemically and biologically important molecules. With these and other advantages, one would have expected NQR investigations to concentrate upon such light elements rather than, for example, on  $^{35}\text{Cl}$ ,  $^{79}\text{Br}$ , and  $^{127}\text{I}$ . The reason that this is not so is that light elements often have low NQR frequencies which hamper their measurement by traditional frequency swept methods. Thus, although the spectra of the halides are difficult to interpret, they are easy to measure. The advent of the nuclear quadrupole double resonance techniques has removed the experimental constraints on the measurements on light nuclei so that they may be expected to dominate the field for some time to come.

### IV. NUCLEAR QUADRUPOLE DOUBLE RESONANCE (NQDR) TECHNIQUES

The theoretical and experimental details of the NQDR techniques are contained in the references. Here we present a brief description of double resonance with level crossing (DRLC) which is the basic technique. We will sketch its advantages over

conventional NQR for light elements and tabulate some of the more sensitive techniques that have developed from DRLC.

DRLC was first described in the unpublished Ph.D. thesis of J. Koo, a student of Prof. E.L. Hahn. The powdered solid specimen needs to include the quadrupolar Q nuclei of interest and an abundant and easily detected assembly of P nuclei which are nearly always protons. The experiment proceeds in cycles with each cycle divided into three phases. During the polarization phase, the sample resides in a large steady magnetic field ( $\sim 1$ T) and after a time of the order of the spin-lattice relaxation time the P nuclei become partially polarized. The sample is then moved to a region of zero field at the same temperature. During the transit, the P nuclei become adiabatically demagnetized to a low spin temperature. The Q nuclei become partially polarized by the P spins when a given pair of quadrupolar split Q energy levels have an energy separation equal to the reduced energy splitting of the P spins as the field is reduced to zero. This PQ spin coupling by exchange of resonant photons is known as level crossing coupling. For simplicity, at this stage we assume that both P and Q spin-lattice relaxation times are long compared with the time the specimen spends out of the large magnetic field.

During the irradiation phase spent in zero applied magnetic field, the Q spins are irradiated at frequency  $\nu$  in an attempt to detect an allowed transition among their quadrupole split energy levels. The P spins are not heated by the irradiation as their energy levels are split only by spin-spin coupling and by much less than  $h\nu$ .

During the final detection phase, the specimen is returned to the large field, during which transit further level crossing occurs. The final spin temperature of the P spins in the large field is sampled by applying a single  $90^\circ$  pulse to the P spins and monitoring the amplitude of the resultant free induction decay. The whole cycle is then repeated with a different value of  $\nu$  until the desired region of the spectrum has been swept. If, during the irradiation phase, the radiation at  $\nu$  appreciably heats the Q spins, some of this energy will be passed back to the P spins by level crossing during the detection phase and the final free induction decay signal of the P spins will be reduced.

No matter which quadrupolar Q spin system is studied, the measurement is always of the P spin

free induction decay. Thus, a simple fixed-frequency spectrometer that can deliver a single  $90^\circ$  pulse to the P spins during each cycle is all that is required.

The technique is particularly suited to light elements with small quadrupole splittings as the sensitivity is almost independent of the size of the quadrupole splitting studied. For example, a good signal-to-noise ratio is obtained for  $^2\text{D}$  at around 100 kHz. The major limitation of the method is that the low field spin-lattice relaxation time of the P spins must be a few seconds or longer so that they do not depolarize during the irradiation phase. This limitation may often be overcome by reducing the specimen temperature sufficiently, although this may necessitate long cycle times in order that the high field polarization phase is sufficiently long to initially polarize the P spins.

Finally, the success of NQDR, and in particular DRLC, in detecting previously undetected resonances, lies in the ability of the P spins to record the cumulative effect of the irradiation of many Q spin resonances during a single cycle. If instead of irradiating at a single frequency  $\nu$ , the frequency is swept during the irradiation phase from  $\nu_1$  to  $\nu_2$ , then, by studying the size of the P spin free induction decay at the end of a single cycle, it is possible to state whether or not there are any Q spin resonances between  $\nu_1$  and  $\nu_2$ . In this manner, Q spin resonances may be rapidly located. Unlike continuous wave NQR, saturation of a resonance does not make it impossible to detect. On the contrary, the use of excessive power merely broadens the line which may help its detection. A final spectrum obtained with low irradiation power, and thus no saturation, reveals the true width and accurate frequency position of the line.

The sensitivity limit implicit in DRLC may be understood as follows. In DRLC, the P spins are affected during the detection phase by the energy which the Q spins can gain from the applied radiation and store during the irradiation phase. Consider two quadrupole split energy levels of the Q spins separated in zero field by an energy  $h\nu$ . A population difference between these two energy levels is created by the level crossing with the P spins that occurs during specimen transit to zero magnetic field at the completion of the polarization phase. If the specimen in zero field is irradiated at frequency  $\nu$ , energy is absorbed until saturation occurs so that the population difference is reduced to zero. After

that, no further energy can be absorbed by the Q spin levels no matter how intense or prolonged the irradiation. Thus, the sensitivity of DRLC depends upon (i) how much polarization is passed to the Q spins and (ii) the number of Q spins relative to the number of P spins. In practice, a ratio of Q to P spins of about 1 to 20 is as low as can be tolerated.

To achieve much higher sensitivity, mechanisms for the continuous transfer of energy between Q and P spins during the irradiation phase must be devised. In this way, the same few Q spins may continuously pass energy to the P spins when the Q spins are irradiated, and the cumulative total of the energy transferred is limited only by the duration of the irradiation phase. This is turn is usually limited by the zero field spin-lattice relaxation time of the P spins,  $T_{1P}(0)$ .

The oldest and to date most used of the very high sensitivity NQDR techniques is double resonance in the laboratory frame (DRLF) invented by Redfield and by Slusher and Hahn following the experiments by Hartmann and Hahn. The PQ spin coupling during the irradiation phase is brought about by applying a radio frequency field to the Q spins with frequency  $\nu_Q$  and a rotating amplitude  $B_1$  and arranging that

$$\gamma_Q B_1 \approx \gamma_P B_L$$

where  $\gamma_Q$  and  $\gamma_P$  are the magnetogyric ratios of the Q and P spins and  $B_L$  is a typical Lorentz internal field acting upon a P spin. In these circumstances, it can be shown that the two spin systems exchange energy by exchange of resonant photons of energy  $h \eta_Q B_1$ . The method is most applicable to nuclei with high  $\gamma_Q$  so that  $B_1$  need not be too large, and to date has mostly been applied to  $^{17}\text{O}$ . The NQR spectra of naturally abundant (0.037%)  $^{17}\text{O}$  may be measured with ease by DRLF in suitable specimens.

A second, more recently introduced, very high sensitivity method is double resonance with coupled multiplets (DRCM). This takes advantage of any splitting in energy that occurs between the doubly degenerate quadrupole split energy levels of half integer spin nuclei due to interaction with neighbouring magnetic nuclei such as protons. To date, it has only been applied to  $^{17}\text{O}$  in natural abundance. The sensitivity is at least that of DRLF, and the irradiation power required is much less. The additional bonus with DRCM is that the  $^{17}\text{O}$  NQR lines display fine structure due to the magnetic near

neighbour interaction which greatly increases the structural information obtained.

The final very high sensitivity technique we shall mention is double resonance with continuous coupling (DRCC) which is applicable to very low (< 500 kHz) frequency spectra and particularly to that of the deuteron. With this technique, the NQR of  $^3\text{D}$  is very easily measured with samples enriched to 1% in deuterium at a given site. In suitable specimens, it is possible to measure the  $^2\text{D}$  spectrum in natural abundance (0.016%).

## V. CONCLUSION

In this paper I have described some of the recent advances in the detection of NQR in light elements. I hope that it has been sufficient to catch the imagination of some students so that they feel it worthwhile to dip into the attached bibliography. To someone in the field, it does seem an exciting and fast moving research topic and holds open the promise that NQR may become for solids what NMR has become for liquids, a very widely used analytical tool.

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