Pure Quadrupole Spectra in Solids[1]

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THE FIRST EXPERIMENTAL OBSERVATION of a pure quadrupole spectrum was made by Dehmelt and Krüger (*1*) in solid *trans*-dichloroethylene at liquid air temperature. A characteristic resonance absorption of radiofrequency energy in the vicinity of 30 Mc was seen for each of the stable chlorine isotopes. Subsequently resonances have been observed in a large number of other chlorine compounds, as well as compounds of other elements. The study of this phenomenon has attracted both chemists and physicists.

The types of studies made at this Laboratory and elsewhere will illustrate some of the applications of the method to chemistry and physics. Even though the field is quite new, no attempt at a complete survey is intended, nor is it implied that all phenomena are completely understood. First, the nature of the phenomenon must be considered in more detail.

The absorption of radiofrequency energy is accompanied by transitions among closely spaced energy levels arising from the interaction of the atomic nuclei with their environment in a solid substance, and the frequency, ν, is determined by $E = h\nu$, E being the energy difference between the levels and h Planck's constant. Hence an explanation of the phenomenon becomes a discussion of the nature of the energy levels involved. This in turn requires some elaboration of the nature of a quantity called the nuclear electric quadrupole moment and the particular features of the nuclear environment that interact with it to determine the levels.

The Energy Levels. Perhaps the most familiar of the nuclear moments are the magnetic (dipole) moment, μ, and the mechanical moment (or intrinsic angular momentum), which is usually designated by a spin quantum number I. In general other magnetic and also electric moments can exist. The electric moments can be treated, for the purposes at hand, by considering the nucleus to be made up of a finitely sized assemblage of charges. One then finds that the electrostatic potential at a point outside the nucleus can be expressed as an infinite series whose successive terms correspond to potentials from certain idealized charge distributions known as higher and higher order electric moments. The first term of this expansion contains the nuclear charge which, in a sense, may be regarded as the simplest electric moment, a mono-pole with dimensions eL^0. The second term in the expansion of a general potential contains the electric dipole moment; however, the theory of nuclear structure implies that there should be no electric dipole moment in nuclei, and to date no experimental phenomenon has been found that requires the existence of such a moment. We are interested in the next term of this expansion which contains the nuclear electric quadrupole moment, Q. This moment has dimensions of eL^2, but it is customary to factor out the protonic charge e and express Q in cm^2. This electric moment is a measure of the departure from spherical symmetry of the nuclear charge distribution. The value for Cl^{35}, for example, is about -0.08×10^{-24} cm^2, the negative sign indicating that the nuclear charge distribution is flattened or oblate with respect to the nuclear-spin axis. A positive sign indicates a prolate distribution. Q differs from zero only for nuclei with $I \geqq 1$.

A quadrupolar nucleus placed in the neighborhood of other electric charges will give rise to an interaction energy, which in general depends on the relative orientation of the nuclear and extranuclear charge systems. This interaction is described in terms of the set of second partial derivatives with respect to coordinates, $q_{ij}; i,j = x,y,z$, of the electrical potential at the location of the nucleus (thus $q_{zz} = \partial^2 V / \partial z^2$, etc.). This interaction results in the quadrupolar nucleus taking a number of allowed orientations in the q_{ij} system, and the energy for each is different. The number of quantum-allowed orientations is determined by the nuclear spin, two being possible for each of the stable chlorine isotopes with $I = 3/2$. The absorption of a quantum of radiofrequency energy by such a system induces a change in orientation from a lower energy configuration to a higher one. The set of second derivatives, which is commonly referred to as the electric field gradient, is a second order tensor quantity. With a proper choice of coordinate axes, the tensor may be represented by three orthogonal components, $|q_{zz}| > |q_{xx}| > |q_{yy}|$, and these conform to Laplace's equation, $q_{zz} + q_{xx} + q_{yy} = 0$. Frequently q_{zz}, the major component of the tensor, is abbreviated by q. The energy of the quadrupolar interaction is often expressed in terms of a parameter called the nuclear electric quadrupole coupling, eqQ, and this parameter is usually evaluated when the phenomenon is observed.

As a simple example, let us consider a quadrupolar nucleus aligned in the field gradient of a single (classical) electron with charge $-e$ at a distance r from the nucleus. The electric potential at the nucleus is

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[1] This work was performed for the Atomic Energy Commission.

$-e/r$ and q_{zz} is $-2e/r^3$. The quadrupole coupling becomes $-2e^2Q/r^3$ and $q_{xx} = q_{yy} = e/r^3$. In this simple case the coupling is said to have axial symmetry. In many physical systems where more complex charge distributions are involved q_{xx} and q_{yy} may not be equal, the asymmetry frequently being denoted by a parameter $\eta = [q_{xx} - q_{yy}]/q_{zz}$.

The energy levels for axial symmetry, $\eta = 0$, are given by $E_m = eqQ[3m^2 - I(I+1)]/4I(2I-1)$ where m may have values $I, I-1, \cdots, -I$. Since m appears only as the square, all levels are twofold degenerate. For $I = 3/2$, the case for all stable chlorine and bromine nuclei, $E_{\pm 1/2} = -eqQ/4$ and $E_{\pm 3/2} = eqQ/4$. With the selection rule $\Delta m = 1$ the transition energy is given by $h\nu = |eqQ/2|$. The quadrupole coupling is often expressed in frequency units and for this case is just twice the observed transition frequency. Since the sign of the coupling is not determined, only its magnitude and the magnitude of q are considered. The case of departure from axial symmetry is considered later. Properties of extranuclear charge distributions giving rise to significant quadrupole couplings are discussed in a later section.

Experimental. Although the mechanism for establishing the energy levels is electric in nature, the main process by which the nucleus absorbs radiofrequency energy in making a transition is magnetic. For this reason the sample is placed in the coil of a tuned circuit of a radiofrequency oscillator where it experiences oscillations in magnetic field. The oscillator is frequency modulated at, say, 100 cps. If the oscillator is now tuned to the frequency of a quadrupole resonance, the oscillator frequency will be swept back and forth through the resonance frequency 100 times a second. Each time the resonance line is crossed, energy is absorbed from the oscillator coil and the circuit is so arranged that the resulting signal can be taken from the circuit, amplified, and presented on the vertical plates of an oscillograph. The horizontal plates of the oscillograph are driven at 100 cps in synchronization with the frequency modulation. Figure 1 is a photograph of a quadrupole line observed in this manner. In this case the line is only a few kilocycles wide. Other electronic arrangements can be used, the principal extension of the technique being the use of a chart recorder and appropriate electronic circuits that allow the line to be seen with a higher signal-to-noise ratio.

Resonance Lines for Chlorine. Each of the stable chlorine isotopes possesses a quadrupole moment, and their resonance lines can be seen in many compounds. If the electrical environment of the nucleus were independent of isotopic substitution, it would follow from the energy level expression that the ratio of observed frequencies for the two stable chlorine isotopes in a given compound should be their quadrupole moment ratio. The ratios given in Table 1 do not vary outside of the accuracy of the frequency measurements. More recent data (*2*) of greater accuracy do, however, show a very small significant variation.

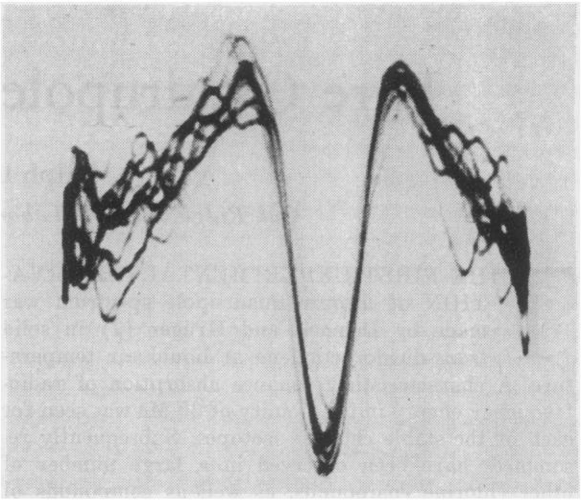

FIG. 1. The 38.254 Mc Cl^{35} line in $CHCl_3$ at 77° K.

Nevertheless, to a very high precision q is a property of the substance that is quite insensitive to isotopic substitution, and accurate quadrupole moment ratios can be determined. Resonance lines for Cl^{35} are much stronger than those for Cl^{37} owing, in part, to the three times greater natural abundance. Frequently just the Cl^{35} lines are measured since the weaker Cl^{37} values can be easily calculated.

Often two or more lines are seen for each chlorine isotope (Tables 1 and 2). A similar effect was first seen and explained by Dehmelt (*3*) for the iodine resonances in SnI_4. The number of lines corresponds to the number of nonequivalent halogen positions in the crystal lattice. Thus each atom experiences a particular q, the magnitude of which depends on the particular lattice position it occupies. The value of q in these substances does not change greatly from one type lattice position to another as evidenced by the close spacing of the multiple lines. Fourteen weak lines were originally seen for CCl_4 (Table 2) and these were measured at 20° K. Later with a more sensitive spectrometer, one of the lines at 77° K was resolved into a doublet, which now gives a total of 15 lines. The crystal structure may be like that of CBr_4 which is reported (*4*) to be monoclinic and of large cell dimensions, apparently with 32 molecules per unit cell. It is likely that there is a sixteenth line in CCl_4 that has not yet been observed.

The frequencies of quadrupole lines shift with temperature changes, in most cases increasing with decreasing temperature. A theory based on a torsional oscillator model has been proposed (*5*) to explain the effect. Briefly the concept is that if there are rapid oscillations (compared to the transition frequency) in the charge distribution, then the effective value of q is an average over the amplitude of these oscillations and is thus of smaller magnitude than that given by the same charge distribution at rest. Thus decreasing the temperature decreases the amplitude of oscillations over which q is averaged, and a higher resonance

TABLE 1

MEASURED FREQUENCIES AND RATIOS FOR SOLID CL COMPOUNDS AT 77° K

Compound	$\nu(Cl^{35})$ Mc	$\nu(Cl^{37})$ Mc	$\nu(Cl^{35})/\nu(Cl^{37})$
$SOCl_2$	32.0908	25.2935	1.26874
	31.8874	25.1331	1.26874
CH_2Cl_2	35.9912	28.3673	1.26876
Cl_2	54.2475	42.7544	1.26882
$CHCl_3$	38.3081	30.1921	1.26881
	38.2537	30.1500	1.26878
$POCl_3$	28.9835	22.8432	1.26880
	28.9378	22.8067	1.26883

TABLE 2

MEASURED FREQUENCIES (MC) FOR CL^{35}

Compound	77° K	20° K	4° K
CCl_4	40.465	40.732	
	40.521	40.794	
	40.540	40.800	
	40.549	40.826	
	40.576	40.831	
	40.587	40.888	
	40.607	40.895	
	40.639	40.918	
	40.643	40.965	
	40.655	40.972	
	40.696	41.022	
	40.721	41.045	
	40.782	41.109	
	40.797	41.139	
	40.817		
CH_3Cl	34.029	34.199	34.206
$AsCl_3$	24.960	25.048	25.054
	25.058	25.158	25.167
	25.406	25.520	25.528
CH_2Cl_2	35.991	36.233	36.243
CCl_3CCl_3	40.761	40.885	
	40.714	40.823	
	40.685	40.798	
	40.551	40.652	

frequency results. At sufficiently low temperatures one would expect excited lattice vibrations to be essentially frozen out, and the resonance frequency would stop increasing with decreasing temperature. The measurements in Table 2 show a moderate frequency increase in cooling from 77° K to 20° K, while further cooling to 4° K gives very little additional increase. Dean and Pound (*6*) have reported higher temperature data on a number of substances. In some cases crystal phase transitions gave discontinuities in a frequency-temperature graph. One compound had four closely spaced lines below the discontinuity while two were present above. Usually the frequency shift at such discontinuities is small, being of the same order as the separations of multiple lines.

Chemistry. Nuclear quadrupole couplings have been determined in a number of gaseous substances by studying hyperfine structure of rotational transitions in the microwave region. Townes and Dailey (*7*) have discussed the origin of q and have shown that it is almost entirely due to the electron distribution in the chemical bond that holds the atom containing a quadrupolar nucleus in the molecule. Their development is based on an atomic orbital model of chemical bonding, and the general features may be applied to solid systems.

Townes and Dailey point out that q has a very large magnitude in many molecules. For example, in many chlorine compounds q must be of the order of 10^{16} esu as determined from magnitudes of observed couplings. A (classical) electron near the nucleus, say at a distance of 1 A, would give a contribution to q over an order of magnitude smaller than the observed 10^{16} esu. A reasonable way to account for such large field gradients is to make use of appropriate atomic orbitals. For example, atomic chlorine has a quadrupole coupling of about (–) 110 Mc from measurements by an atomic beam experiment (*8*). The closed electron shells have spherical symmetry and do not contribute to q. The outer shell, however, lacks a p electron, and it is this departure from spherical symmetry that gives q a large value. In this case a deficiency of a p electron from a full shell may be regarded as similar to a surplus of a p electron. It is the net unbalance in p orbitals that matters. A p electron is so effective because of its nonspherical angular distribution near the nucleus (penetrating orbital). Electrons described by s type wave functions do not contribute to q because of the spherical symmetry of s states. The coupling found in solid chlorine at 20° K is only 0.7 per cent lower than the atomic beam value. This has been taken as an indication that the chemical bond in Cl_2 uses essentially a pure p atomic orbital with very little if any s hybridization. If the bonding orbitals could be better described by a mixture of s and p orbitals, there would be less *net unbalance* in the electron distribution about the chlorine nuclei and q would be smaller.

If the chlorine atom in the example above were converted to an ion by adding an electron, it would have a noble gas configuration with no unbalance in the electron distribution about the nucleus, and q should be zero. If, following Pauling (*9*), a bond to chlorine with partial ionic character is considered, the foregoing concepts lead usually to the correlation of reduced couplings with increased ionic character. Thus couplings found for many solid inorganic chlorine compounds where there is a moderate amount of ionic character (BCl_3, $AsCl_3$, $SnCl_4$, $SiCl_4$, PCl_3, etc.) generally are lower than the more covalently bonded organic chlorides ($CHCl_3$, CCl_4, etc.). An interesting example of a reversed type of ionic character is in ClF which has a coupling much higher than Cl_2. In this case there may be contributions from the resonant structure $Cl^+ F^-$, and the ionic character is in the direction of increasing the departure from spherical symmetry in the charge distribution about the chlorine nucleus. Finally, if a partial double bond is formed, the coupling will be lowered. For example, if an atom is bonded with essentially a sigma p orbital, q will have a large magnitude. If there is also partial double bond character through the use of pi p orbitals, there

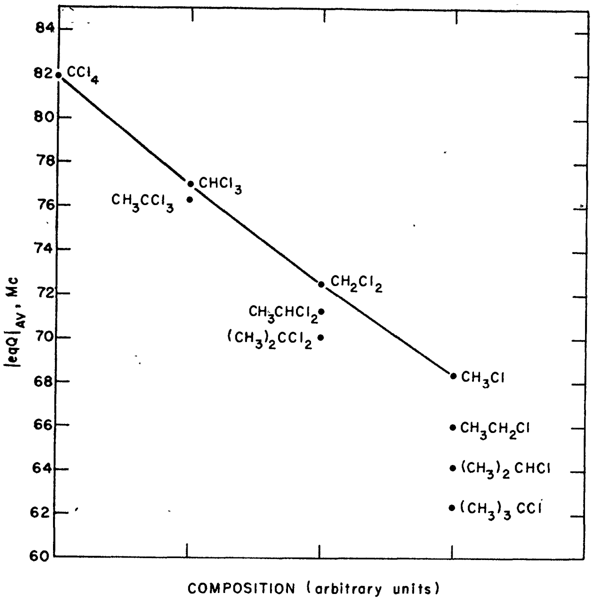

FIG. 2. Cl^{35} quadrupole couplings in alkyl chlorides at 20° K.

will be some contributions to q from this source. These contributions are properly represented by tensors. One effect of the pi contribution is to give a tensor element that subtracts from the magnitude of the major element (q_{zz}) of the sigma contribution. The net effect is a decreased coupling. A second effect of the pi contribution is to give asymmetry to the coupling, $\eta \neq 0$. This effect will be briefly mentioned later.

The chloroethanes (Fig. 2) show a coupling decrease each time a Cl atom is replaced by H. Replacement of H atoms by CH_3 groups results in further systematic coupling decreases. Here the coupling is taken as twice the observed transition frequency, the average frequency being used in cases where closely spaced multiple lines are seen. The coupling trend may be explained in terms of variations in the amount of ionic character in the bond. For example, the more chlorine atoms per molecule the less the ionic character in each C–Cl bond and the higher the coupling. The interpretation is consistent with the general chemical properties of the substances involved. Additional correlations have been made on several chloroethanes, and in each case the coupling trend may be reasonably explained by considering the electronegativities of the atoms involved and their effect on the C–Cl bond ionic character. The one carbon Freons have been correlated in a similar manner, but in this case the use of an additional parameter, partial double bond character, was used. Pauling (*9*) first proposed this concept ($F^-C = Cl^+$ resonant structures) to explain bond lengths in the Freons. Measurements have recently been made on several corresponding bromine and iodine compounds (*10*), and there is a striking parallelism in trend. A few of these include the coupling in CH_2Br_2 which is appropriately higher than CH_3Br while CH_3CH_2Br is lower. Moreover the value in $CH_3CH_2CH_2Br$ is very close to CH_3CH_2Br, very similar to the corresponding chlorine cases. Comparisons of solid values with microwave gas values show good agreement in several cases and marked departures, up to 10 per cent, in others. Although the solid values are for molecular crystals where the intermolecular interactions are presumably weak, the comparisons seem to suggest a change in the nature of the bond in going from the gaseous to the solid state. One of the large problems is to properly interpret the role of lattice effects. Townes and Dailey (*11*) have interpreted the quadrupole data on solid iodine in the light of its crystal structure. They conclude that in addition to the main molecular covalent bond, there are two weak intermolecular bonds to each atom.

The Zeeman Effect. Bersohn (*12*) has given a theoretical treatment of nuclear quadrupolar systems both in the absence and presence of a magnetic field. A magnetic field will remove the twofold degeneracy of the quadrupolar levels and in principle allow a larger number of lines (Zeeman components) to be observed. In order to illustrate the phenomenon a simple case will be considered. The energy levels and allowed transitions for chlorine ($I = 3/2$) in the presence and absence of an applied magnetic field are indicated in Fig. 3. The magnitude of the magnetic splitting (spacing of Zeeman components) depends on the magnetic field strength, H, and the angle, θ, between the direction of the magnetic field and q_{zz}. We will consider the coupling to have axial symmetry, $\eta = 0$. For an arbitrary angle θ and for $I = 3/2$, a single quadrupole line will split into four Zeeman components symmetrically displaced about the original frequency. For special values of θ some of the lines coincide. Only two lines are present for $\theta = 90°$ and three lines for $\theta = 54°44'$, the central line coinciding with the frequency of the unsplit quadrupole line. A powder sample gives a random spread in values for θ, and the application of a magnetic field merely causes the line to broaden and, with high enough field, become undetectable.

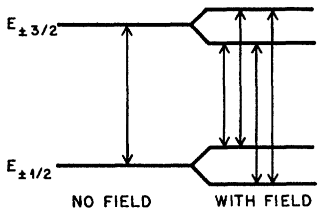

FIG. 3. The nuclear electric quadrupole energy levels for chlorine, with and without an applied magnetic field.

Let us consider the Zeeman effect in a single crystal of sodium chlorate (*10*). The crystal structure (*4*) is cubic with four molecules in the unit cell, and all chlorine atoms occupy equivalent lattice positions. In the absence of a magnetic field a single quadrupole resonance for Cl^{35} appears at about 30 Mc. The four ClO_3^- ions in the unit cell have a pyramidal configuration with a threefold axis of symmetry, and these

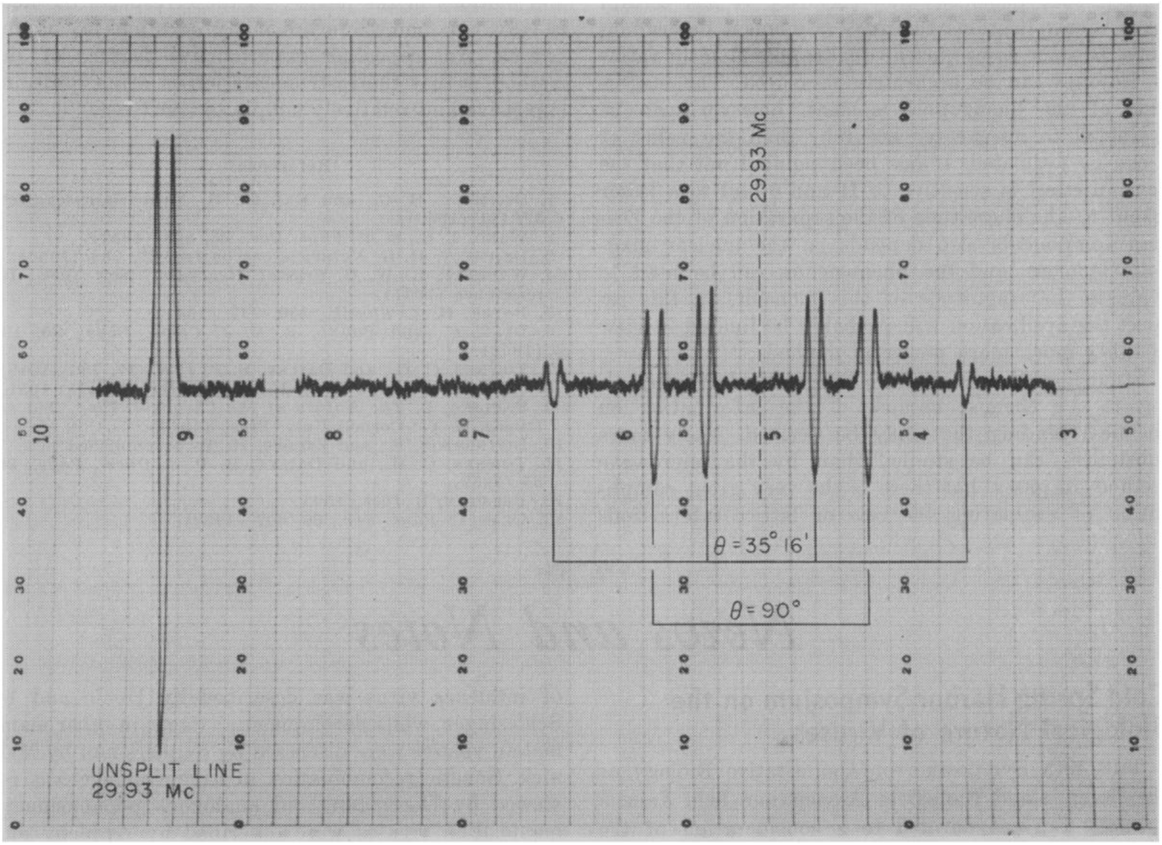

FIG. 4. Quadrupole resonance in a $NaClO_3$ single crystal without an applied magnetic field (left) and with a field of approximately 50 gauss applied along a twofold axis of the cube.

axes lie along the directions of the four body-diagonals of the cube. The direction of q_{zz} for each lies along these symmetry axes, and from crystal symmetry $\eta = 0$. Thus each chlorate ion has its own field gradient system, equivalent except for direction, and the application of an external magnetic field will, in general, give a separate set of four Zeeman components for each of the four chlorine atoms. The nature of the splittings will depend on the orientation of the magnetic field with respect to the diagonals of the cube. If the field is oriented normal to a face of the cube, it makes an angle of 54°44′ with each of the diagonals, and all four sets of Zeeman components are superimposed. A total of three lines are present since this special angle gives a three line pattern.

Figure 4 is a recording of the Zeeman components for Cl^{35} in sodium chlorate with a field of approximately 50 gauss oriented along a face diagonal (twofold axis) of the cube. The field direction makes an angle of 90° with two of the body diagonals giving two components and an angle of 35°16′ with the other two diagonals giving four more components. A recording is also shown for the unsplit quadrupole line. The second derivative of the absorption line is recorded.

Asymmetry in the Field Gradient Tensor. A measurement of η, the departure of the coupling from axial symmetry, often allows more to be understood about the chemical substance. In the previously mentioned study of the intermolecular bonding in solid iodine (*11*) η was one of the important parameters. If the coupling is not axially symmetric a different expression must be used for the energy levels (*12*). The magnitude of η can be evaluated directly from the pure quadrupole spectrum for all spin cases except $I = 3/2$. For example, the energy levels of the iodine nucleus ($I = 5/2$) with $\eta = 0$ give rise to two lines, one having exactly twice the frequency of the other. However, if $\eta \neq 0$ the ratio is not 2:1, and the actual ratio can be used to evaluate the asymmetry. Dean (*13*) has demonstrated that the asymmetry can also be evaluated for the $I = 3/2$ case by performing a Zeeman experiment. He observed the chlorine resonance in a single crystal of *p*-dichlorobenzene in the presence of a constant magnetic field. By carefully studying the line frequencies with different orientations of the crystal in the magnetic field he was able to locate the directions of the principal axes in the crystal and evaluate q and η. He indicated that the asymmetry could be due to double bond character in the C–Cl bond.

Quadrupole spectroscopy is a field that has attracted both physicists and chemists. It has certain areas of applications for nuclear moment determinations. In some cases nuclear quadrupole moment ratios of isotopes can be accurately measured. The magnitude of the quadrupole moment, however, can be evaluated to no greater accuracy than the value of q can be estimated. It has been pointed out that the Zeeman effect is sensitive to H and θ and to a lesser extent η. The magnitude of the separation of the Zeeman components also depends on the nuclear magnetic moment, and the phenomenon can be used to evaluate the magnitude of this moment. In this respect the application will probably be limited in view of other much more powerful methods.

Studies on the nature of q are particularly appealing to the chemist because of the information on chemical binding that may be derived. Many more substances can be studied than by the microwave method on gases, but there is the very great complication of evaluating the role of lattice interactions and motions in the lattice. In these respects the field is very new and there are many questions to be answered. An appealing experimental feature of the method is that the instrumentation is often quite inexpensive and relatively simple to construct.

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News and Notes

Cold Spring Harbor Symposium on the Biological Nature of Viruses

THE 18th Symposium on Quantitative Biology of the Long Island Biological Association, held June 5 through 11, was devoted to a consideration of the biological nature of viruses, and of the interactions between viruses and their host cells. M. Delbruck opened the Symposium with an outline of the program, in which he distinguished and defined three states of viruses, the infective, vegetative, and provirus states. In the infective state the virus is extracellular, metabolically inert, resting between cycles of reproduction. It is extracellular virus which has been most extensively studied by physical, chemical, and immunological techniques, and which is best known because of its accessibility. It is however of less interest to biologists than the intracellular states in which the virus demonstrates some of the properties of a living organism. In the vegetative state, the virus is intracellular, virus reproduction occurs, genetic changes of the virus take place, and the host cell metabolism is so disorganized that the pathology of virus diseases is produced. In the provirus state, the virus coexists with its host cell in a symbiotic relationship in which the virus assumes the *de facto* role of a genetic unit of its host cell. The provirus protects its host cell against the attack of related viruses, profoundly affects the genetics of its host cell, and is a natural method for the storage and preservation of viruses.

Evidence for the existence of the vegetative state in bacteriophages was presented by Doermann, and the stages in its maturation to the infective state were discussed by Levinthal. The intracellular development of influenza virus was described by Henle and by Schlesinger, while developmental stages in other mammalian viruses were discussed by Sanders and by Melnick. Genetic recombination in bacteriophage was reviewed by Doermann, and analogous phenomena in mammalian viruses were described by Appleby and by Hirst, and a paper on this subject by Burnet was read by Fenner. The striking similarities between bacteriophages and animal viruses were made apparent, as well as the extraordinary difficulty of studying animal viruses by the usual techniques.

The properties of the provirus state in lysogenic bacteria were discussed by Bertani, including genetic interactions with related viruses and the protective effect of provirus against host cell destruction by related viruses. Bertani suggested that the prophage may be attached to some chromosome-like structure in the bacterial nucleus and so divides with it in cell duplication. Experiments on the inheritance of prophage lambda in crosses of *E. coli* K12, reported by Appleyard, were consistent with this hypothesis. The conditions involved in the transition from infective phage to prophage were discussed by Bertani and by Lieb. The physiological state of the host cell, the temperature, and the multiplicity of infection are important factors, as well as the genetic constitutions of host cell and virus. The transition from provirus to the vegetative state, the phenomena of induction, was described by Jacob, who suggested that the primary event is a local disturbance in the bacterium which dislodges the prophage from its locus on the bacterial chromosome so as to permit its uncontrolled multiplication. Evidence suggesting that genetic recombination in bacteria may be mediated by an agent analogous to a virus was presented by Hayes. This