The above calculations indicate that only about one-third or one-half the K-shell ionization can be attributed to internal conversion. The remaining ionization is probably the direct result of the emission of the alpha-particle.

Assuming that the excess K-shell ionization is due to the direct action of the alpha-particle as it leaves the atom, the probability of this process is given by the quantity N_K/N_α multiplied by the fraction of K-shell ionizations not due to internal conversion. Using our values for N_K/N_{800} and N_K/N_α together with the value $\alpha_K = 0.053 \pm 0.013$, we arrive at

$$(2.2\pm0.4)\{1-(0.053\pm0.013)/(0.15\pm0.028)\}\times10^{-6} = (1.4\pm0.35)\times10^{-6}$$

for the probability of K-shell ionization by the alpha-particle.

Migdal[9] has made theoretical calculations of the probability of ionization of the daughter atom by a particle which leaves the nucleus. Migdal's theory predicts that the alpha-particle almost always ionizes the atom, but that the ionization probability of a given electron shell decreases rapidly as shells nearer and nearer the nucleus are considered.

The process of direct ionization by the alpha-particle has been suggested as the origin of the L x-rays which are observed in Po^{210} radiations.[10,11]

The approximations made in Migdal's calculations include the use of perturbation theory to describe the effect of the alpha-particle, the assumption that the alpha-particle moves with uniform velocity as it leaves the nucleus, and the use of nonrelativistic hydrogen-like wave functions to describe the atom. These approximations are best in the case of K-shell ionization, but even here the error may be appreciable. Migdal's result for the probability of ionization of the K-shell is 2.2 $(137\ v_\alpha/Z^2c)^2$, where v_α is the velocity of the alpha-particle and Z is the atomic number of the daughter atom. Evaluation of this expression gives 2.6×10^{-6} in the case of Po^{210}.

Migdal's theory thus agrees in order of magnitude with the experimental results, $(1.4\pm0.35)\times10^{-6}$, but the predicted ionization probability is too high to be reconciled with either our results or those of Grace *et al.*[2] Since Migdal's theory neglects the effects of screening of the nucleus from the K electrons, one might argue that the Z in Migdal's theory should be replaced by a smaller "effective" Z. This change would make the predicted ionization probability even higher and thus would increase the discrepancy with experiment. The authors believe that approximations in Migdal's theory may result in an overestimate of the K-shell ionization process.

The authors would like to express their appreciation to Professors R. Hofstadter and W. E. Meyerhof for their valuable suggestions and criticisms concerning this work.

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[9] A. Migdal, J. Phys. (U.S.S.R.) 4, 449 (1941).
[10] I. Curie and F. Joliot, J. phys. et radium 2, 20 (1931).
[11] W. Rubinson and W. Bernstein, Phys. Rev. 82, 334 (1951).

PHYSICAL REVIEW VOLUME 86, NUMBER 3 MAY 1, 1952

The Sign of the Quadrupole Interaction Energy in Diatomic Molecules*†

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(Received January 9, 1952)

The molecular beam magnetic resonance method has been used to determine the sign (and the magnitude in those cases where it has not been previously measured) of the quadrupole interaction energy of the alkali nuclei in the homonuclear molecules, that of Na^{23} and Li^7 in the alkali halides, and that of Cl^{35} and Cl^{37} in KCl. An obstacle is inserted into the path of the beam so that its edge coincides with the position of the undeflected beam. Molecules of either positive or negative total magnetic moment are then removed from the beam which arrives at the detector. Certain maxima in the nuclear resonance spectrum at high magnetic fields ($eqQ \ll g_I\mu_0H$) arising from the transitions $\Delta m_I = \pm1$ are suppressed depending on the states removed by the obstacle. It is thus possible to identify the resonance maxima in terms of the transitions which produce them. From this evidence the sign of the quadrupole interaction energy can be deduced. The quadrupole interaction energy, eqQ, is positive for Li^7 and negative for Na^{23} in the homonuclear and the halide molecules. These results suggest that the sign of q at a given nucleus is the same in a rather considerable range of diatomic molecules. The interaction constant, eqQ, is positive for Cs^{133} in Cs_2, and negative for K^{39} in K_2, Rb^{85}, Rb^{87} in Rb_2, and Cl^{35}, Cl^{37} in KCl. The signs of the interaction for K^{39}, Rb^{85}, Rb^{87}, and Cs^{133} in the alkali fluorides, and for Cl^{35}, Cl^{37} in TlCl as determined by the molecular beam electrical resonance method are the same as those for the same nucleus in the molecules here considered.

INTRODUCTION

It is the purpose of the present paper to discuss in detail a method which permits the determination of the sign of the quadrupole interaction energy in diatomic molecules and to present the results of new measurements on the sign and the magnitude of the quadrupole interaction energies of several nuclei in a considerable range of diatomic molecules. A preliminary description of the method has previously been given.[1]

Unfortunately it is not possible, in general, to deduce

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* This research was supported in part by the ONR.
† Submitted by R. A. Logan in partial fulfillment of the requirements for the degree of Doctor of Philosophy, in the Faculty of Pure Science, Columbia University.

[1] P. Kusch, Phys. Rev. 76, 138 (1949).

the sign and magnitude of the electric quadrupole moment of a nucleus from a knowledge of the quadrupole interaction energy of the nucleus in a particular molecule. The only completely unambiguous exception is in the determination of the quadrupole moment of the deuteron from the experimental value of the quadrupole interaction of the deuteron in HD and D_2. In this case the molecular wave functions are sufficiently well known to permit an exact calculation[2] of q.[3] In the case of the molecule Li_2, Foley[4] has made a calculation of q from the Bartlett-Furry wave functions. These wave functions[5] lead to a dissociation energy and an internuclear distance for Li_2 which agree with the experimentally observed quantities but the extent of their validity in the calculation of q is uncertain. In other cases where the quadrupole interaction has been measured, good wave functions are not available for the determination of q, but in some instances apparently satisfactory approximations have been devised.[6]

The present results themselves do not, therefore, permit a direct determination of either the sign or the magnitude of the nuclear quadrupole moment. They do, however, indicate certain systematic behavior of the quadrupole interaction energy and may thus aid in establishing the validity of the various models and approximations proposed for the determination of the nuclear electric quadrupole moment from observed interaction energies.

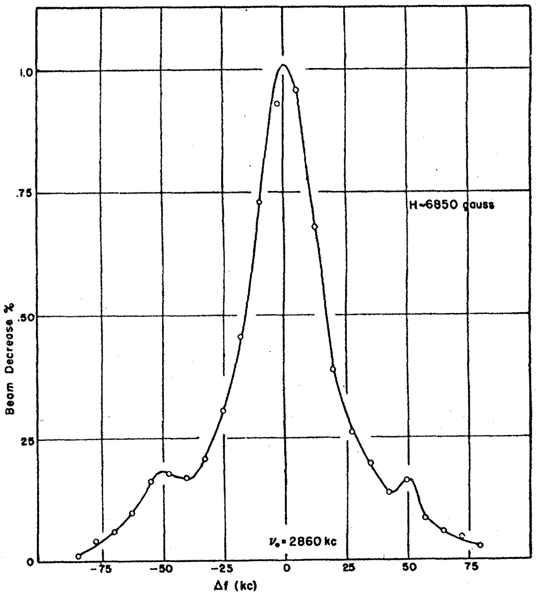

FIG. 1. Nuclear resonance spectrum of Cl^{35} in KCl.

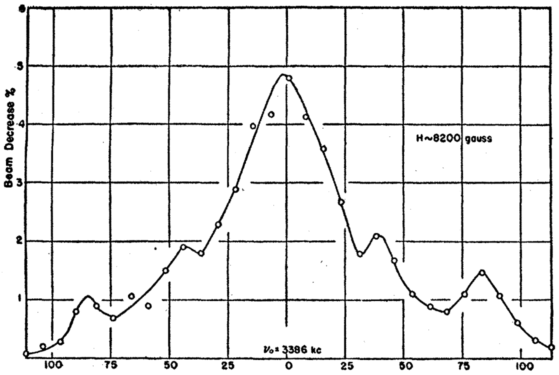

FIG. 2. Nuclear resonance spectrum of Rb^{85} in Rb_2.

THEORY

In the present experiments the high field spectrum arising from a nuclear reorientation in a diatomic molecule is observed. This spectrum has been discussed in detail by Feld and Lamb[7] and by Nierenberg and Ramsey[8] for a diatomic molecule which contains one nucleus possessing both a magnetic dipole moment and an electric quadrupole moment and another nucleus of spin zero. The conclusions are, however, valid for an arbitrary diatomic molecule including the homonuclear molecule[9] when J is large and when the electric quadrupole interaction is large compared to the magnetic interaction between nuclei and that between each nucleus and the field caused by the molecular rotation. All of these criteria are substantially satisfied by the molecules here considered.

The spectrum consists of a series of $2I$ maxima. When I is an odd half-integer, the central peak in the spectrum corresponds to the nuclear resonance frequency, $\nu_0 = g_I\mu_0 H/h$, and is not, at sufficiently high magnetic fields ($g_I\mu_0 H \gg eqQ$), affected by the quadrupole interaction. The width and shape of the central maximum is determined by the interaction of the nuclear moment with the magnetic field due to the molecular rotation and by the resolution effects of the apparatus. The other maxima appear as satellites of the central peak and their position is determined by the magnitude of the quadrupole interaction as given by Feld and Lamb.

A typical high field resonance spectrum when $I = 3/2$ is that of Cl^{35} in KCl, shown in Fig. 1. For the magnetic

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[2] A. Nordsieck, Phys. Rev. **58**, 310 (1940).

[3] The q employed here was suggested by J. Bardeen and C. H. Townes, Phys. Rev. **73**, 97 (1948), and represents directly the gradient of the electric field at the nucleus in the inward direction along the internuclear axis. This definition of q ascribes a physical significance to the previously defined q' of A. Nordsieck, Phys. Rev. **58**, 310 (1940). The q used by B. T. Feld and W. E. Lamb, Jr., Phys. Rev. **67**, 15 (1945), is expressed in terms of coordinates relative to an axis fixed in space, whereas Nordsieck's q' is expressed relative to a coordinate system fixed in, and moving with, the molecule. These definitions are related by

$$q_{\text{Bardeen-Townes}} = 2eq' = -[(2J+3)/2J]2eq_{\text{Feld-Lamb}}$$

where e = proton charge, J = rotational quantum number.

[4] A calculation by H. M. Foley quoted in reference 1.

[5] J. H. Bartlett, Jr., and W. H. Furry, Phys. Rev. **38**, 1615 (1931).

[6] C. H. Townes and B. P. Dailey, J. Chem. Phys. **17**, 782 (1949).

[7] B. T. Feld and W. E. Lamb, Jr., Phys. Rev. **67**, 15 (1945).

[8] W. A. Nierenberg and N. F. Ramsey, Phys. Rev. **72**, 1075 (1947).

[9] H. M. Foley, Phys. Rev. **71**, 747 (1947).

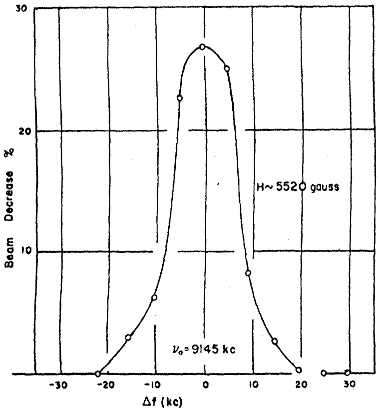

FIG. 3. Nuclear resonance spectrum of Li^7 in Li_2.

fields employed the interaction energy of the nuclear magnetic moment is large compared to the quadrupole interaction energy and genuinely high field conditions prevail. The frequency separation between the two maxima is $eqQ/4h$ and from Fig. 1 and other data it is found that $eqQ/h=0.420$ Mc. When $I=5/2$, as in the case of Rb^{85}, whose spectrum in Rb_2 is shown in Fig. 2, two auxiliary maxima appear on each side of the central maximum. In this case $eqQ/h=1.10$ Mc. In both cases the rapidly varying intensity of other components of the spectrum in the neighborhood of the satellite have the effect of shifting the maximum to the center so that the stated value of eqQ/h represents a lower limit of the quantity. This effect is especially pronounced in the case of Rb^{85} in Rb_2 where the low abundance (<0.5 percent) of molecules in a beam of rubidium evaporated from an oven makes necessary the use of low resolution (which arises due to a large amplitude of rf field) to obtain observable intensities in the spectral envelope. Typical spectra when $I=3/2$ are also shown in Figs. 7 and 8.

A case of special interest is the resonance of Li^7 in Li_2 shown in Fig. 3. In this case the quadrupole interaction is not sufficiently great to resolve the satellites from the central maximum in view of the limited resolving power of the apparatus (natural width of an isolated line in $Li_2 \sim 3.6$ kc) and in view of the effect of the $\mathbf{I}\cdot\mathbf{J}$ interaction in broadening the envelope. The observed envelope, nevertheless, differs in shape from that observed for Li^6 in LiI shown in Fig. 4, where quadrupole effects are known to be negligible.[10] As will be shown later, there is considerable evidence to indicate that there is, in fact, an unresolved quadrupole structure in this envelope and that a reasonable estimate of the quadrupole interaction energy may be obtained on the basis of the assumption that the satellite maxima determine the half-width of the observed pattern.

A detailed quantitative description of the shapes of the resonance curves requires the inclusion of several effects not considered by Feld and Lamb. Among these are the cosine interaction between nuclear spin and molecular rotation, the variation of q with both rotational and vibrational quantum number, the effect of a J, which is small for a not inappreciable fraction of molecules in the beam, and the resolution properties of the apparatus. However, for the purpose of a determination of the sign of the quadrupole interaction energy, these effects do not modify the conclusions which may be deduced from observed data by the use of the simple Feld-Lamb theory.

The spectrum, at high magnetic fields, which occurs as a consequence of a nuclear reorientation in a diatomic molecule, cannot directly yield information about the sign of the quadrupole interaction energy. The observed pattern is entirely symmetrical about the central frequency, ν_0, and it is not possible to identify the satellite maxima in terms of the transitions $\Delta m_I=\pm 1$ which produce them. It will be shown, however, that the removal from the beam of molecules with states of positive or negative m_I gives rise to an asymmetry in the resonance spectrum which permits a determination of the sign of eqQ.

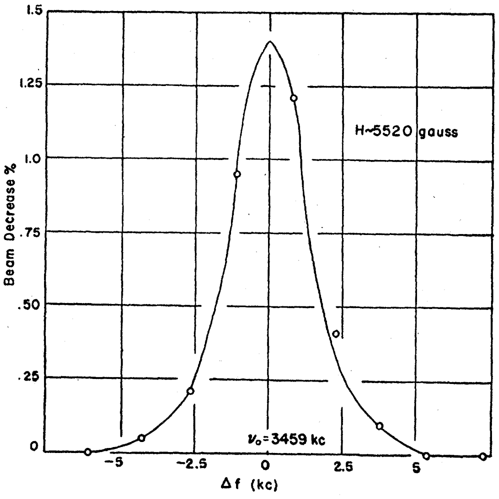

FIG. 4. Nuclear resonance spectrum of Li^6 in LiI.

The portion of the expression for the energy levels of a diatomic molecule at high magnetic fields ($eqQ \ll g_I\mu_0 H$) which depends on m_I is:

$$W=m_I g_I \mu_0 H - \frac{eqQ[3m_J^2-J(J+1)][3m_I^2-I(I+1)]}{4(2J+3)(2J-1)I(2I-1)} - c m_I m_J.$$

The first term is the interaction energy of the nuclear magnetic moment with the applied magnetic field, H, the second term the interaction energy of the nuclear electric quadrupole moment, Q, with the gradient, q, of the electric field at the nucleus and the third term the interaction energy of the nuclear magnetic moment

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[10] P. Kusch, Phys. Rev. 75, 887 (1949); N. A. Schuster and G. E. Pake, Phys. Rev. 81, 157 (1951).

with the magnetic field produced by the molecular rotation. Feld and Lamb have shown that the transitions $\Delta m_I = \pm 1$ lead to maxima in the envelope in the region near $m_J = 0$. In this region the quantity $[3m_J^2 - J(J+1)]$ is negative, and except for constant terms and the small term cm_Im_J,

$$W = m_I g_I \mu_0 H + \text{constant}(eqQm_I^2).$$

The ordering of the energy levels is determined by the first term of the expression. The various possibilities when $I = 3/2$ are shown in Fig. 5. When g_I is negative, it is evident that the high frequency satellite maximum will correspond to the transition $(-3/2 \leftrightarrow -1/2)$ if eqQ is positive and to the transition $(1/2 \leftrightarrow 3/2)$ if eqQ is negative. The situation is reversed if g_I is positive. The sign of the interaction can thus be determined by an identification of the satellite maxima in terms of the m_I values of the terminal states if the sign of g_I is known.

Since the trajectory of a molecular beam through the sequence of magnets and slits in the molecular beam apparatus is determined by the magnetic moment of the molecule, it is possible, by the introduction of suitable obstacles in the trajectories of the molecules, to exclude from observation molecules in which m_I is either positive or negative and hence to affect the intensity distribution in the resonance spectrum.

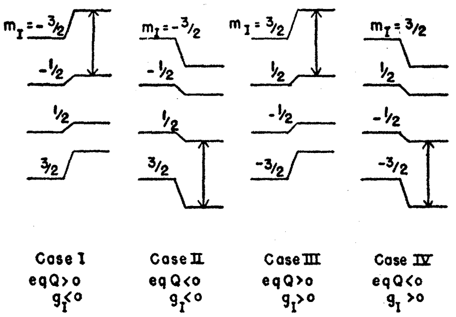

FIG. 5. Detail of nuclear energy level diagram ($I = 3/2$) showing the shift in energy due to the quadrupole interaction energy for the four cases depending on the relative signs of eqQ and g_I. In each case the arrow indicates the transition which gives rise to the high frequency satellite in the nuclear resonance spectrum.

METHOD

A schematic diagram of the apparatus used in these measurements is shown in Fig. 6. The apparatus, except for the presence of the obstacle between the B and C magnets, is a typical molecular beam apparatus used for the observation of molecular spectra arising from a nuclear reorientation. Refocusing occurs at the detector when the molecule is in the same state in both the A and B magnets; if a transition occurs in the C magnet there will, in general, be a change in magnetic moment and refocusing will not occur.

The beam is a narrow ribbon in the xz plane and is propagated in the positive x-direction from the oven to the detector. The field in the A, B, and C magnets may be either along the positive or negative y-direction, but is in the same direction in all three magnets. The ratio $(\partial H/\partial y)/H$ in the A and B fields is determined by the shape of the magnet pole faces and is a fixed and generally unalterable property of the apparatus, so that the direction of $\partial H/\partial y$ is reversed when the direction of H is reversed. Hence a particle with a positive component of magnetic moment along H is deflected while passing through the A-field in the positive y-direction, independent of the field direction. The net deflection of the beam at the collimating slit is equal to zero and beyond the collimating slit all molecules of positive moment will have a positive y-coordinate.

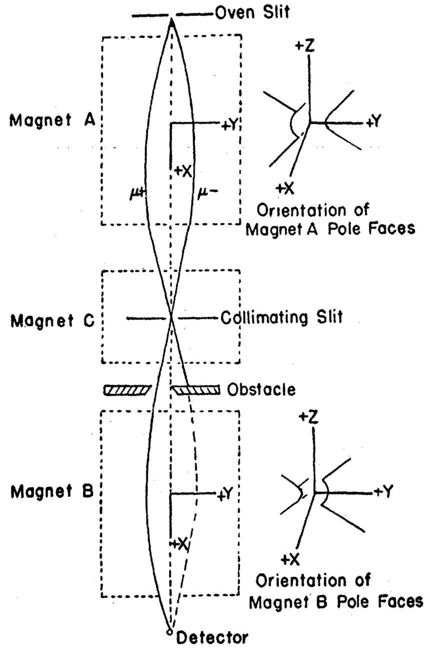

FIG. 6. Schematic diagram of the apparatus showing the arrangement of the magnet pole faces.

An obstacle with a sharp edge, parallel to the other elements which define the beam (source slit, collimating slit and detector) may be interposed between the B and C magnets. If the obstacle is in the region of $+$ y-coordinate and if its edge coincides with the position of the undeflected beam, all particles with a positive component of resultant moment in the A field are removed from the beam which arrives at the detector. In the event that transitions occur in the C region, the spectrum which is observed will not contain lines resulting from transitions for which the initial state is characterized by positive moment.

In the present case we are concerned with diatomic molecules in which there is no net electronic angular momentum, and the magnetic fields employed in the experiments are large ($\approx$10,000 gauss) so that the angular momentum vectors are completely decoupled. The resultant magnetic moment is contributed by the two nuclear moments μ_{I1} and μ_{I2}, and the rotational

TABLE I. Table of allowed values of the total magnetic moment of Li^7I^{127}, in nuclear magnetons, in the direction of the applied field, for the possible m_I of the Li^7 and I^{127} nuclei.

$m_I(I^{127})$ $m_I(Li^7)$	5/2	3/2	1/2	−1/2	−3/2	−5/2
3/2	6.065	4.942	3.818	2.694	1.570	0.447
1/2	3.894	2.771	1.641	0.523	−0.601	−1.724
−1/2	1.724	0.601	−0.523	−1.641	−2.771	−3.894
−3/2	−0.447	−1.570	−2.694	−3.818	−4.942	−6.065

moment μ_J. The effective moment of the molecule is then:

$$\mu = -(m_{I1}g_{I1} + m_{I2}g_{I2} + m_Jg_J)\mu_0.$$

In all cases considered in these experiments, the nuclear g values are negative so that each nucleus contributes a positive moment for a positive value of m_I. The contribution of μ_J to the moment may be ignored since g_J is sufficiently small in comparison with g_I so that $|m_Jg_J| \ll |m_Ig_I|$. For any m_{I1} and m_{I2}, the moment distribution is affected symmetrically by μ_J since positive and negative values of m_J are equally probable. The effect is to broaden the deflection spectrum at any point in a manner analogous to, though not identical with, that produced by the velocity distribution.

The degree to which molecules in which a given nucleus has a positive (or negative) component of moment in the direction of the field can be separated from the beam depends on the relative values of the two nuclear moments in the molecule. The removal from the beam of nearly all molecules in which μ_{I1} contributes a positive moment requires that $|\mu_{I2}| \ll |\mu_{I1}|$ so that the sign of the magnetic moment of the molecule is determined predominantly by the orientation of μ_{I1}. When this condition holds, the interposition of the obstacle as described above will leave the observable intensity of a line arising from transitions between two states of negative m_{I1}, unaltered, between two states of positive m_{I1} zero, and between two states with m_{I1} of opposite sign, one-half of the original intensity. It is evident in this case that the selective removal of molecules with positive (or negative) m_{I2} cannot be achieved.

As an example, consider the case of Li^7I^{127}. The spin and magnetic moment of the nuclei are, respectively, 3/2, 3.256 nm for Li^7 and 5/2, 2.809 nm for I^{127}. Table I exhibits the possible values of the component of the magnetic moment of Li^7I^{127} in the direction of the applied field. It is evident that if all molecules whose component of magnetic moment in the field direction is positive, are removed from the beam which arrives at the detector, then the central maximum $(1/2 \leftrightarrow -1/2)$ in the nuclear resonance spectrum of Li^7 in Li^7I^{127} will be reduced in intensity by 1/2, while the satellite maximum $(3/2 \leftrightarrow 1/2)$ will be reduced in intensity of 1/6 of its original value and that due to the transitions $(-1/2 \leftrightarrow -3/2)$ will have 5/6 of its original intensity. By this means the satellite maxima are identified in terms of the transitions which produce them, and from this evidence the sign of the quadrupole interaction can be deduced.

As long as $eqQ \gg c\bar{J}$, where $\bar{J}$ is the most probable value of J, it is not necessary that the satellite maxima be resolved from the central peak in order to allow the determination of the sign of the quadrupole interaction energy. The large density of levels near $m_J/J=0$ gives rise to the satellite maxima, and these maxima contribute directly to the intensity distribution in the unresolved resonance envelope. The removal of molecules containing m_I of a particular sign will suppress the satellites unsymmetrically, and will produce a shift in the center of the observed resonance spectrum. A detailed example of this effect in the Li^7 resonance in Li_2 is given in a later section. When $c\bar{J} \gtrsim eqQ$, the maxima in the envelope of the satellite lines become very poorly defined, and when the whole spectrum is unresolved, a detectable shift in the center of the pattern may not occur when molecules containing m_I of a particular sign are removed from the beam.

APPARATUS

The molecular beam apparatus was originally built in 1947. The design is symmetrical about the collimating slit which is located at the center of the homogeneous C-field. The inhomogeneous A and B fields have equal lengths (50.8 cm) and equal ratio of field gradient to field $(\partial H/\partial y)/H = 8\ \text{cm}^{-1}$. The pole pieces on the deflecting magnets are made of Permendur which has a saturation value considerably in excess of 20,000 gauss. The over-all length of the apparatus from the oven slit to the tungsten detector wire is 175.8 cm. For a gradient of 1.6×10^5 gauss/cm and at an oven temperature of 900°K, a fairly typical temperature in the

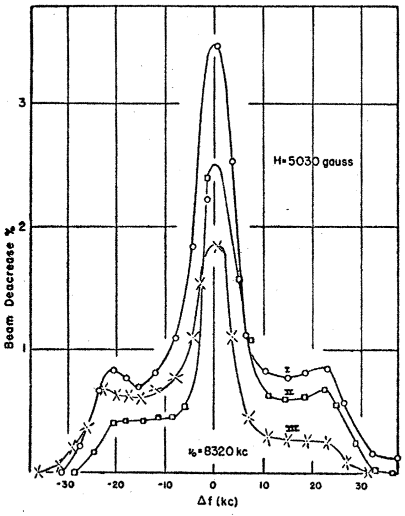

FIG. 7. Nuclear resonance spectrum of Li^7 in LiI; curve I is obtained with full beam, curve II with molecules of positive total moment removed from the beam, and curve III with molecules of negative total moment removed from the beam.

production of beams of the alkali halides,

$$S_\alpha = 5.77\times10^{-3}g \text{ cm}$$

where S_α is the deflection of a molecule at the detector which has undergone a transition resulting in a moment change $g_I\mu_0$ and where α is the most probable velocity in the oven. For Cl^{35} ($g_I = 0.55$ nm), $S_\alpha = 3.2\times10^{-3}$ cm. The actual change in intensity at the detector which is observed when a transition occurs is determined by the widths of the various defining elements. If the oven slit, collimating slit, and detector each have a width of 2.5×10^{-3} cm the maximum drop in intensity at the detector which may be observed when Cl^{35} undergoes a transition is about 38 percent. Actually, in the cases under consideration, the probability of transition, averaged over the velocity distribution of the molecules, cannot exceed 0.7; a particular nuclear species may have less than 100 percent isotopic abundance, and population in a great number of states (J, m_J) may broaden the spectrum so that the actual observed intensity change may be very much less than the calculated maximum.

The obstacle consists of two parallel quartz edges which are mounted parallel to the z-direction. This structure is movable in the y-direction and can be used to cut the beam on the side of either positive or negative y-coordinate. The obstacle is located between the B and C magnets as shown in Fig. 6. Evidently the optimum position at which to mount the obstacle is at a point in the B magnet where the maximum dispersion occurs in the deflection spectrum of the various molecular moments. However, the introduction of a movable slit at some point along the length of the B magnet leads to considerable mechanical complications. At the position of the actual obstacle, just before the entrance to the B field, a molecule is subject to deflections by the A field only. When $(\partial H/\partial y)_A = 1.44\times10^5$ gauss/cm, a molecule containing an atom of Li^7, and with velocity α, propagated from an oven at a temperature of 900°K, is deflected 5.3×10^{-3} cm when $m_I = 3/2$ and 1.8×10^{-3} cm when $m_I = 1/2$ due to the Li atom only.

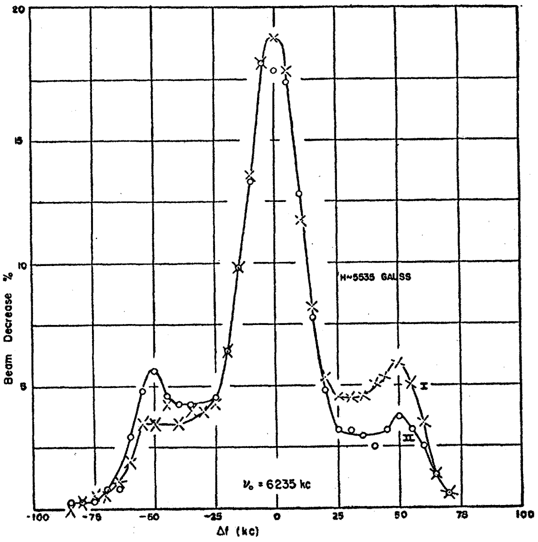

FIG. 8. Nuclear resonance spectrum of Na^{23} in Na_2; curve I is obtained with molecules of negative total moment removed from the beam and curve II with molecules of positive total moment removed from the beam.

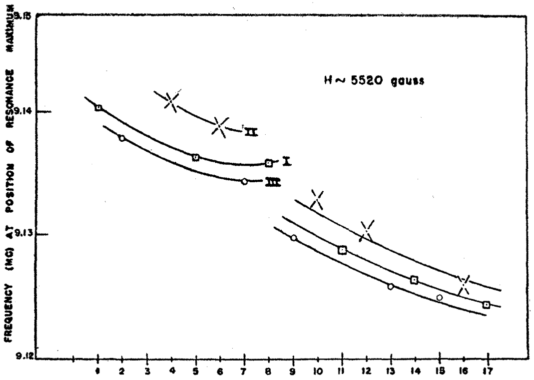

FIG. 9. Successive determinations of the center of the resonance spectrum of Li^7 in Li_2; curve I is obtained with full beam, curve II with molecules of positive total moment removed from the beam, and curve III with molecules of negative total moment removed from the beam.

The insertion of the obstacle into the beam path makes the beam intensity at the detector more sensitive to mechanical distortion of the apparatus since there are then four elements which define the beam instead of the usual three, and in addition, the umbra or region of constant maximum beam intensity at the detector is reduced in width by the presence of the obstacle. Observation of the resonance spectrum is also made more difficult by the reduction of beam intensity which arises when the obstacle is inserted. Changes in beam intensity of the order of 0.01 percent may be observed under good conditions; it is, nevertheless, difficult to obtain the envelope of a spectrum with sufficient accuracy to make an exact quantitative analysis of the intensity distribution.

RESULTS

The nuclear resonance spectrum of Li^7 in LiI is shown in curve I of Fig. 7 while curve II shows the same resonance when the obstacle removes molecules of positive total moment from the beam, with the consequent suppression of the low frequency satellite. It is thus evident that the low frequency satellite corresponds to the transitions $(1/2\leftrightarrow3/2)$ indicating that eqQ is positive. Curve III exhibits the converse effect where molecules of negative total moment have been removed from the beam which arrives at the detector, with the consequent reduction of the intensity of the high frequency satellite.

The observed nuclear resonance spectrum of Na^{23} in the homonuclear molecule Na_2 in which molecules of negative total moment are removed by the obstacle is shown in curve I of Fig. 8. The partial removal of the low frequency satellite shows that eqQ is negative. The converse effect is exhibited in curve II where molecules of positive total moment have been removed from the beam with the consequent suppression of the high frequency satellite.

In the nuclear resonance spectrum of Li^7 in the homonuclear molecule Li_2 the satellite maxima are unresolved. However, the sign of the quadrupole interaction energy is determined unambiguously by observing the position of the center of the resonance when molecules of either positive or negative total moment are removed from the beam by the obstacle. The suppression of the high frequency satellite in this manner shifts the center of the observed resonance in the direction of lower frequency and vice versa. In Fig. 9, a plot is made of successive determinations of the position of the center of the resonance curve for various positions of the obstacle in each of two separate runs. A slow downwards drift in field is evident from the curves by the slow decrease in ν_0. Curve I indicates the successive positions of the center of the resonance obtained with full beam; when molecules of total positive moment are removed, the center of the resonance is shifted to higher frequency as shown in curve II indicating that the transitions $(3/2\leftrightarrow 1/2)$ give rise to an unresolved low frequency satellite. The converse effect is exhibited in curve III where molecules of total negative moment are removed from the beam and the center of the resonance is shifted to lower frequency, indicating that the high frequency satellite has been suppressed. This identification of the satellite maxima in terms of m_I indicates that eqQ is positive.

The observed shift of the resonance center of about 1.5 kc on inserting the obstacle can be seen to be quite reasonable by the construction of an approximate resonance spectrum from the three component line envelopes. When $I=3/2$, the frequency of the satellite maximum $(3/2\leftrightarrow 1/2)$ for $eqQ\ll g_I\mu_0 H$ is

$$\nu=(g_I\mu_0 H/h)+[eqQ(3z^2-1)/8h]+(czJ/h)$$

where $z=m_J/J$ and $0\leqslant|z|\leqslant 1$. Neglecting the last term, the component lines extend over a frequency range defined by $z=0$ at the maximum to $z=\pm 1$ at the other limit, and $z=\pm 1/\sqrt{3}$ at the central frequency ν_0. Since the number of transitions in any frequency interval is proportional to the Δz required to cover the interval, the ratio of the satellite area on the side of ν_0 containing the maximum to the area on the other side of ν_0 is $1/(\sqrt{3}-1)=1.37$. Hence we may represent the satellite by a right triangle having its right-angled vertex at $\nu_1=\nu_0-eqQ/8h$ and with the base of the triangle extending from ν_1 to $\nu_2=\nu_0+eqQ/4h$. The area distribution is adjusted by the addition of a very small triangle adjacent to the right-angled vertex. The central structure $(1/2\leftrightarrow -1/2)$ is represented by an isosceles triangle having an area equal to 4/3 that of the satellite, since the total probability of the central line is greater than that for the satellites by this factor. Applying resolution corrections for the natural resonance width of 3.6 kc, and assuming a central half-width of 8 kc and $eqQ/4h=16$ kc, a resonance curve of half-width equal to that of the observed resonance curve was obtained. A similar construction was made in which the component maxima were reduced in intensity corresponding to the removal by the obstacle of molecules of total positive moment. The center of the resonance thus obtained was displaced about 1 kc from ν_0, which agrees fairly well with the observed shift of about 1.5 kc. The result obtained here for the sign of eqQ for Li^7 in Li_2, and the value of q calculated using available molecular wave functions yield a positive value for Q.

Since the positive Q for Li^7 is in contradiction with the predictions of simple nuclear models, an attempt has been made to obtain an independent determination of the sign of $Q(\mathrm{Li}^7)$ by a study of LiH. A more dependable value of q may be calculated for LiH than for Li_2, since better wave functions are available. Since on heating, LiH dissociates before sufficient vaporization occurs to produce a molecular beam, various schemes for synthesizing Li and H in a molecular beam oven were tried without success. The detailed experimental investigation[11] of the thermal dissociation properties of LiH, however, indicates that it is not feasible to produce a beam of LiH in a molecular beam apparatus. At the high oven temperature necessary to vaporize the lithium it is impossible to introduce sufficient hydrogen into the oven to produce a reasonable amount of LiH and still maintain the necessary vacuum in the apparatus.

The magnitude of the quadrupole interaction is determined by the separation $eqQ/4h$ of the satellite maxima when $I=3/2$. In the case of Li^7 in LiI the separation of the observed satellite maxima shown in Fig. 8 yields the result $eqQ/h=172$ kc. In the case of the resonance of Li^7 in Li_2 the two satellite maxima which determine the magnitude of the interaction were unresolved. If the assumption is made that the unresolved satellite maxima determine the half-width of the envelope then $eqQ/h=+60$ kc is found. This assumption is apparently quite reasonable in view of the agreement achieved above in explaining the displacement of the resonance caused by the insertion of the obstacle, where it was assumed that $eqQ/h=64$ kc. A similar situation arises in the case of the Cs^{133} resonance in Cs_2 where $I=7/2$ and the 6 satellite maxima were unresolved. It was assumed that the half-width of the resonance spectrum was determined by the satellites $(3/2\leftrightarrow 5/2)$ and $(-3/2\leftrightarrow -5/2)$ which gives the value $eqQ/h=+0.23$ Mc. The estimate is, of course, quite crude and a large $\mathbf{I}\cdot\mathbf{J}$ interaction might make the estimate of doubtful validity.

The magnitude and sign of the quadrupole interactions that have been determined by the methods

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[11] Private communication from Johnson, Hill, and Perlow.

described above and by the electrical resonance method are listed in Table II.

DISCUSSION

The invariance of the sign of the quadrupole interactions of each of the two nuclei, Li^7 and Na^{23}, in the homonuclear molecules and all the halides; of K^{39}, Rb^{85}, Rb^{87} and Cs^{133} in the homonuclear molecules and the fluorides and of Cl^{35} and Cl^{37} in KCl and TlCl suggests that the sign of q, the gradient of the electric field at the nucleus, is the same in a large range of diatomic molecules.

The sign of q is known[2] to be positive in the hydrogen molecule. Recent work[12] has shown that the quadrupole moment, Q, of both chlorine isotopes is negative, and this result applied to the present data indicates that q at the Cl nucleus in KCl and TlCl is positive. Finally, Foley[4] has shown that q is positive at the Li nucleus in Li_2. This result is, of course, less certain than the other two results because of a possible inadequacy in the wave functions used in the calculation.

A positive value of q at one nucleus in a diatomic molecule occurs when the gradient contributed by one nucleus exceeds in magnitude that contributed by the net electronic configuration. The net electric field at the nucleus is, of course, equal to zero. A positive value of q corresponds to a minimum of the electrostatic potential at the nucleus in question. It is an attractive possibility that q at each nucleus in every diatomic molecule is positive. No general theorems have been proved to substantiate this conjecture; however, in the three cases where a test has been made, q is positive and it follows that q is positive in all diatomic molecules in which the signs of the quadrupole interactions of Li and Cl have been determined. It is certain that if the sign of q is reversed in a molecule containing another nucleus, it is reversed in all molecules, here considered, containing that nucleus.

Townes, Foley, and Low[13] have proposed a model which predicts the signs of the quadrupole moments of the nuclei. The sign of the moment of Li^7 is explicitly predicted to be negative and that of K^{39} positive. From the curve presented by these authors, the sign of $Q(Na^{23})$ is positive, though the sign is read from a dotted and presumably doubtful portion of the curve. The model makes no predictions as to the sign of the quadrupole moment of Rb^{85}, Rb^{87}, and Cs^{133}.

TABLE II. Magnitude and sign of the quadrupole interaction constant eqQ/h.

Molecule	eqQ/h (Mc)	Reference to sign of eqQ	Reference to magnitude of eqQ
Li^7 resonance			
Li_2	$+0.060$		
LiF	$+0.408$		[a]
LiCl	$+0.192$		[a]
LiI	$+0.172$		[a]
LiBr	$+0.184$		[a]
Na^{23} resonance			
Na_2	-0.423		[b]
NaF	-8.12		
NaCl	-5.40		[c]
NaI	-3.88		[c]
NaBr	-4.68		[c]
K^{39} resonance			
K_2	-0.158		[b]
KF	-7.938	[d]	[d]
Rb^{85} resonance			
Rb_2	-1.10		
RbF	-70.31	[e]	[e]
Rb^{87} resonance			
Rb_2	-0.580		
RbF	-34.00	[e]	[e]
Cs^{133} resonance			
Cs_2	$+0.23$		
CsF	$+1.240$	[f]	[f]
Cl^{35} resonance			
KCl	-0.420		
TlCl	-15.795	[g]	[g]
Cl^{37} resonance			
KCL	-0.336		
TlCl	-12.446	[g]	[g]

[a] P. Kusch, reference **10**.

[b] Kusch, Millman, and Rabi, Phys. Rev. **55**, 1176 (1939).

[c] See reference 8.

[d] L. Grabner and V. Hughes, Phys. Rev. **79**, 819 (1950).

[e] V. Hughes and L. Grabner, Phys. Rev. **79**, 314 (1950).

[f] J. W. Trischka, Phys. Rev. **74**, 718 (1948).

[g] Carlson, Lee, and Fabricand, Phys. Rev. **85**, 784 (1952).

From the data presented in the present paper, the predictions of Townes, Foley, and Low lead to a negative value of q in Li_2 and at the Li nucleus in the lithium halides. This result is opposite to that calculated by Foley.[4] Similarly a negative value of q is predicted at the sodium and potassium nuclei in diatomic molecules. The value of q at the Cl nucleus in the chlorine bearing molecules is positive. While no direct evidence exists to indicate that q cannot, in fact, show this variation, it is nevertheless true that an estimate of the sign of q from a model of nuclear structure and from the sign of the interaction energy eqQ cannot be accepted without reservation.

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[12] V. Jaccarino and J. G. King, Phys. Rev. **83**, 471 (1951).

[13] Townes, Foley, and Low, Phys. Rev. **76**, 1415 (1949).