Sign of the Quadrupole Interaction of Li^6 in LiCl†

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The sign of the quadrupole interaction energy of Li^6 in LiCl has keen found to be positive. Previous determinations have shown that the quadrupole interaction energy of Li^7 in the same molecule is also positive. It may, therefore, be concluded that both of the stable isotopes of lithium have a quadrupole moment of the same sign, though the sign itself is not known.

THE signs of the quadrupole interaction energies of certain of the alkali atoms in the homonuclear diatomic molecules and in some of the alkali halides have been determined[1,2] by a method which involves the selection of states of either positive or negative magnetic moment for observation by the molecular beam magnetic resonance method. The sign of the quadrupole interaction energy (eqQ) does not, of course, yield information as to the sign of the electric quadrupole moment, Q, of the nucleus. Considerable uncertainty exists[3] in determination of the sign of $Q(\text{Li}^7)$ from the data on $(\text{Li}^7)_2$ because of the limited accuracy of the electronic wave functions of Li$_2$ in the determination of the gradient, q, of the electric field at the Li nucleus. Nevertheless, both the sign and the magnitude of the ratio of the quadrupole moments of two isotopic nuclei can be determined unambiguously from a measurement of the sign and magnitude of the quadrupole interaction energies in the same molecule, since q is very closely the same for both isotopes. The magnitude of the ratio of the quadrupole moments $|Q(\text{Li}^6)/Q(\text{Li}^7)|$ has been found[4] to be 0.023 ± 0.002, but the sign of the ratio has not previously been determined. In LiCl $(eqQ)_7=192$ kc/sec, so that, in the same molecule, $(eqQ)_6=4.4$ kc/sec.

In the work of Feld and Lamb,[5] the high field resonance spectrum of Li^6 or any other nucleus of spin 1 in a diatomic molecule is shown to consist of two intensity distributions resulting from the transitions $m_I=1\leftrightarrow m_I=0$ and $m_I=0\leftrightarrow m_I=-1$, whose maxima are symmetrical about the frequency $g_I(\text{Li}^6)\mu_0H/h$ and are separated from each other by a frequency interval of $3eqQ/8h$, which is here 1.7 kc/sec. The spectrum is actually observed[6] as a single unresolved maximum with a half-width of 5.5 kc/sec. The lack of resolution can be accounted for solely in terms of the natural half width of the separate lines which compose the spectrum since in the presently available apparatus with a transition length of 28 cm over which the rf amplitude is applied, the natural half-width is 2.2 kc/sec. The

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width of the resonance spectrum is, in addition, increased by the distribution within a finite frequency interval of the lines which contribute to the spectrum, both because of the quadrupole interaction and because of an interaction between the nuclear magnetic moment and the magnetic field arising from the molecular rotation.

The determination of the sign of the quadrupole interaction energy depends on a redistribution of intensity within the spectrum when states characterized by either positive or negative m_I are removed from a molecular beam. It is possible, by presently available methods, to select molecules characterized by either a total positive or a total negative magnetic moment. In order that this selection should be effective in selecting states in which the moment of the nucleus in question is either positive or negative, it is necessary that the other nucleus which comprises the diatomic molecule have a relatively small magnetic moment. Clearly, the the only lithium halide in which the Li^6 nucleus gives a major contribution to the total molecular magnetic moment is LiCl. In all the other halides of Li,^{6} the preferential removal of states in which the moment of Li^6 is, say, positive, is extremely inefficient.

The preferential removal of states of positive m_I by an obstacle is limited by the small magnetic moment of the Li^6 nucleus. At the position of the obstacle in the present apparatus the width of the beam is about 4×10^{-3} cm and the deflection of an Li^{6}Cl^{35} molecule of maximum moment and velocity α the most probable velocity in the oven, is 2.9×10^{-3} cm. Accordingly, since the deflection pattern is comparable in width to the beam itself, a reduction in the intensity of the total beam to half of its original value by interposition of the obstacle from one side of the beam has only a limited effect in removing molecules characterized by a magnetic moment of a particular sign. A detailed calculation for Li^{6}Cl^{35} for the particular conditions of these experiments indicates that interposition of an obstacle to the center of the undeflected beam from the side of the beam on which m_I for Li^6 is positive, decreases the populations of states for which m_I is $+1$ from 1 to 0.28, that of states for which m_I is 0 from 1 to 0.50 and that of states for which m_I is -1 from 1 to 0.72.

The calculation of line intensities from the popula-

tions of the states is subject to a considerable uncertainty. If it is assumed that the two components of the spectrum are independent, the intensities of the components are proportional to the sums of the population of the terminal states; in the case here discussed the intensities of the lines $1 \leftrightarrow 0$ and $0 \leftrightarrow -1$ are then 0.78 and 1.22 respectively. As a further approximation it is possible to assume that each of the two components can be represented by the usual resonance curve with a width at half-intensity of 5.0 kc/sec. The superposition of two such curves, whose centers are separated by 1.7 kc/sec and of relative intensities 0.78 and 1.22, yields a maximum which is shifted by about 0.22 kc/sec from the maximum obtained by the superposition of two curves of equal intensity. Since the shift may be reversed in sign by interposition of the obstacle into the beam from the side on which m_I is negative, a total displacement of the maximum by 0.44 kc/sec when the obstacle is shifted from one side of the beam to the other may be anticipated.

Because of the considerable overlapping of the two components of the pattern there will be a competition for the $m_I = 0$ state. In the limiting case, when at any frequency the probability of transition to $+1$ and -1 is equally great, the relative intensities of the two components are 0.53 and 0.97. An estimate of the shift of the maximum as the obstacle is moved from one side of the beam to the other is then 0.54 kc/sec. It is to be noted that the spectrum becomes slightly unsymmetrical in shape when the beam is partially cut. The center of the intensity distribution is here determined at a point midway between two points of $\frac{3}{4}$ the maximum intensity, since such a determination can much more readily be made experimentally than can a determination of the point of maximum intensity. The difference between the center as here determined and the true maximum is very small and is much less than the errors introduced by the approximations of the model.

The nuclear resonance of Li⁶ in LiCl has been observed at a field of about 3100 gauss. At this field the Li⁶ nucleus is wholly decoupled from the molecular rotation and the high-field treatment of Feld and Lamb is completely applicable. The experimental arrangements have been discussed previously.[2] For the present purposes, LiCl in which the Li⁶ was enriched to 95.2 percent was used. With this sample, the Li⁶ resonance had a maximum depth of about 13 percent of the beam and it was possible to determine the center of the resonance with considerable accuracy.

The experimental procedure is to reduce the intensity of the beam at the detector to some fraction of its original value by interposing an obstacle first on the side of the beam on which the total moment is positive and then on the side on which it is negative. The frequency of the center is determined in each case by observation of points of equal intensity on either side of the center of the resonance. During a run a small
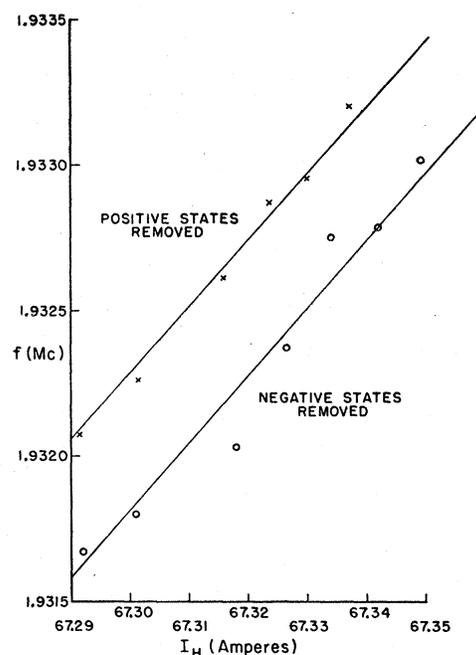

FIG. 1. The frequency of the center of the Li⁶ resonance in LiCl as a function of field current as states of either positive or negative m_I are selectively removed from the beam.

drift in the field may occur which may give rise to a frequency shift between successive observations comparable to the shift arising from the selection of states. It is obviously possible to avoid significant error by a sufficiently long sequence of observations. The result of a typical run is shown in Fig. 1, where the frequency of the resonance center is plotted as a function of the current in the magnet coils as the beam is alternately cut from the two sides to one half of its full intensity. The data indicate that $(eqQ)_6$ is positive, as for the quadrupole interaction energy of Li⁷ in the same molecule. Other data taken under different experimental conditions in which the direction of all fields in the apparatus was reversed and in which the fraction of the beam removed by the obstacle was varied give the same clear result as that shown in Fig. 1, both in the magnitude and the sign of the shift. A number of runs made with LiCl with a normal abundance of Li⁶ also give a positive $(eqQ)_6$, though the data are inferior to those obtained with the enriched sample. The mean shift observed in enriched LiCl, where the data are good, when the beam was cut to one-half of its full value is 0.44 kc/sec, in excellent agreement with that obtained from the approximate calculations.

While a small variation of q may be expected between the molecules of LiCl of different isotopic constitution because of a small variation of the internuclear distance, this variation can hardly be of sufficient magnitude to reverse the sign of q. The consistency of the shift observed in these experiments with the ratio $|Q_6/Q_7|$ found by Schuster and Pake[4] from

observations on $LiAl(SiO_3)_2$ offers experimental evidence that q is not markedly different for a molecule containing Li^6 or Li^7. It is, therefore, concluded that the sign of the quadrupole moment of Li^6 is the same as that of Li^7. Previous data obtained by the method of molecular beams have been able to give only an upper limit for $|Q_6/Q_7|$. The present data indicate that Q_6 is other than zero and give at least a rough quantitiative verification of the result of Schuster and Pake of the value of $|Q_6/Q_7|$.

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Change in the Inversion Spectrum of ND₃ from Resonant to Nonresonant Absorption*

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The absorption due to the inversion spectrum of ND_3 centered near 1600 Mc/sec was measured at pressures from 0.3 to 80 cm Hg in the frequency interval 1100 to 2600 Mc/sec. The inversion frequency was found to decrease with increasing pressure and became substantially zero at about 9 cm Hg. This change occurs at pressures about 15-fold lower than for NH_3, a result in accord with Margenau's theory. At the higher pressures where the absorption is of the nonresonant or Debye type, the collision diameter is about 6.9A, a value roughly one-half that associated with resonant absorption at low pressures.

1. INTRODUCTION

COLLISION broadening in the microwave inversion spectrum of NH_3 near 24 000 Mc/sec has been studied extensively, both at pressures below 1 mm Hg where the considerable fine structure is completely resolved and at higher pressures where the lines become so broad that this structure is completely obliterated. Working in the pressure region from 10 cm Hg to several atmospheres, Weingarten[1] and Bleaney and Loubser[2] found that the unresolved spectrum could be represented by a single Van Vleck-Weisskopf line shape factor provided empirical values were chosen for the line width and resonance frequency. They showed that the resonance frequency decreased as the pressure was increased and became substantially zero for pressures above two atmospheres. The line width was found to rise much less rapidly than the pressure in the transition region, but, as shown by the more detailed experiments of Bleaney and Loubser, to become proportional to the pressure above four atmospheres. The effective collision diameter appeared to change from an initial value in the neighborhood of 13A to about 7.7A at the higher pressures, a change which was attributed to the effect of multiple collisions.

A similar behavior is to be expected for the completely deuterated ammonia ND_3 which in its ground vibrational state has an inversion resonance near 1600 Mc/sec.[3,4] However, on the basis of the theoretical treatment of Margenau,[5] the shift in the inversion frequency should occur at pressures about 15-fold lower than in the case of NH_3. In this event the effect of multiple collisions on the spectral broadening process should be relatively unimportant.

Measurements of the absorption in ND_3 were made at a number of pressures between 0.3 and 80 cm Hg in the frequency interval 1100 to 2600 Mc/sec. The results are in accord with the predictions from Margenau's theory. A definite shift in frequency is evident at a pressure as low as 1 cm Hg. Above 9 cm Hg the inversion frequency has become effectively zero and the transition from resonant to nonresonant or Debye absorption is virtually complete.

2. EXPERIMENTAL

A hybrid mode cylindrical cavity,[6] tunable by a movable center post from 1100 to 2600 Mc/sec, was used as the gas absorption cell. Over this frequency range the loaded Q of the empty cavity varied from 3000 to 5000. The absorption coefficient of the gas was determined as described previously[7,8] from the cavity response curve displayed on an oscilloscope. At the lower pressures the absorption was obtained from the initial Q and relative power transmitted by the cavity. At the higher pressures the absorption was also obtained from measurements of the Q's of the empty and gas-filled cavity.

Calibrated attenuators were used to obtain the law of the crystal detector several times throughout the course of the investigation. The power level at the

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