PHYSICAL REVIEW VOLUME 90, NUMBER 1 APRIL 1, 1953

Low Frequency Resonances in the Spectra of Diatomic Molecules*

R. E. Coté† and P. Kusch
Columbia University, New York, New York

(Received December 22, 1952)

The molecular beam magnetic resonance method has been used in the study of some previously unobserved resonances in NaF, NaCl, NaBr, NaI, and KBr. The frequency and intensity distribution within the resonance spectra have been studied at zero external field and the dependence of both the frequency and the shape of the resonance spectra on external magnetic field has been determined. At zero field these resonances fall in the frequency range from 0 to 157 kc and occur because of a quadrupole interaction and from a cosine interaction between I and J. At sufficiently high field, the frequency of the maxima of the resonances is $2g_I\mu_0H/h$. The lines are ascribed to a transition between the levels $F=J+\frac{1}{2}$ and $F=J-\frac{1}{2}$. In most respects the lines fulfill theoretical predictions; the frequencies of the lines at zero magnetic field, however, deviate considerably from those predicted from other data.

INTRODUCTION

Both the molecular beam magnetic and electric resonance methods have been used[1–5] in a study of the internal interactions within a diatomic molecule and of the interaction of the molecule with externally applied fields. The present paper reports the application of the molecular beam magnetic resonance method to the observation of certain previously unobserved lines in the spectra of several diatomic molecules and presents a theoretical analysis of these lines.

Feld and Lamb[6] have given an analysis of the effect of a nuclear quadrupole moment on the energy levels of a diatomic molecule in a $^1\Sigma$ state in a magnetic field. They discuss spectra due to transitions, $\Delta m_I=\pm 1$, $\Delta m_J=0$, at high fields and $\Delta F=\pm 1$ at low or zero fields. Since, in general, a large number of vibrational and rotational states is occupied, the spectrum is very rich in lines. In the most common cases it is not possible to observe individual lines and an important element of the theory is the statistical analysis of the density of the lines in the spectrum. Although FL consider the case in which one of the nuclei has a spin, I_2, of 0 they state that the results are valid for the more general case in which both nuclei may have quadrupole moments. The injection into the theory, of a cosine coupling of the nuclear spin to the molecular angular momentum was shown by Nierenberg and Ramsey,[1] to explain the otherwise anomalous widths of the fluorine resonances in LiF and CsF.

To simplify the presentation of relevant theory and since the present experiments deal only with molecules which contain a nucleus for which $I_1=\frac{3}{2}$, we shall limit our discussion to that case. For our purposes a line will be defined as the envelope of the unresolved components of a spectral distribution.

The analysis proposed by FL, of the spectrum of the simple molecule (I_2 is 0, the rotational angular momentum of the molecule, J, is large, and the cosine coupling of I and J is negligible) in zero external field predicts the appearance of a single line whose frequency is determined solely by the magnitude of the quadrupole interaction and whose width is determined by the resolution properties of the apparatus. Certain lines, observed for the alkali halides by NR, had approximately the correct frequency as determined from high field observations on the same molecules, but their widths and shapes could not be ascribed to the resolution properties of the apparatus. The extension of the theory as given by NR includes an $\mathbf{I}\cdot\mathbf{J}$ term in the Hamiltonian; the calculation is carried to terms in $1/J$ and therefore considers the effect of finite values of J. Three lines are predicted in the weak field spectrum arising from the transitions $F=J+\frac{3}{2}\leftrightarrow F=J+\frac{1}{2}$, $F=J-\frac{1}{2}\leftrightarrow F=J-\frac{3}{2}$, and $F=J+\frac{1}{2}\leftrightarrow F=J-\frac{1}{2}$. The first two of these form a close doublet, the separation of whose components is determined by the magnitude of the coefficient of the $\mathbf{I}\cdot\mathbf{J}$ interaction term. Zeiger and Bolef[5] observed this splitting in the zero field lines of Cl^{35} in TlCl^{35}. They have analyzed the shape of the envelope of the spectrum with the inclusion of all the known interactions and the effects of a finite J. Large residual differences between the calculated shapes after an adjustment of constants, and the observed spectra are attributed to a variation with vibrational and rotational quantum numbers of the gradient of the electric field at the nucleus.

The third line resulting from the transition $F=J+\frac{1}{2}\leftrightarrow F=J-\frac{1}{2}$ has not been observed previously although it has been discussed by Ramsey.[7] Observations of this previously unobserved line are presented for the first time in the present paper. As will be shown, the frequencies of the components of the line at zero field

---

* This research was supported in part by the U. S. Office of Naval Research. Submitted by R. E. Coté in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University.

† Present address: Pratt and Whitney Aircraft Corporation, East Hartford, Connecticut.

[1] W. A. Nierenberg and N. F. Ramsey, Phys. Rev. **72**, 1075 (1947), hereafter referred to as NR.

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

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

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

[5] H. J. Zeiger and D. I. Bolef, Phys. Rev. **85**, 788 (1952).

[6] B. T. Feld and W. E. Lamb, Jr., Phys. Rev. **67**, 15 (1945), hereafter referred to as FL.

[7] N. F. Ramsey, Phys. Rev. 74, 286 (1948).

depend on the quadrupole interaction through terms in $1/J$ and on the cosine interaction through terms in J. At fields which are somewhat greater than zero, but far less than the field at which the interaction energy of the nucleus with the applied field is comparable to the energy of interaction of the nuclear quadrupole moment with the gradient of the electric field at the nucleus, the intensity maximum of the line is found at about twice the usual nuclear resonance frequency, $g_I\mu_0 H/h$.

THEORY

The Hamiltonian which determines the energy levels of a diatomic molecule in a magnetic field is:

$$\mathcal{H}=-\frac{eqQ[3(\mathbf{I}\cdot\mathbf{J})^2+\frac{3}{2}(\mathbf{I}\cdot\mathbf{J})-I(I+1)J(J+1)]}{2I(2I-1)(2J+3)(2J-1)} +c\mathbf{I}\cdot\mathbf{J}+g_I\mu_0\mathbf{I}\cdot\mathbf{H}+g_J\mu_0\mathbf{J}\cdot\mathbf{H}. \quad (1)$$

This expression does not include any interactions involving the second nucleus within the molecule. The first term is the electric quadrupole interaction energy and is expressed in the notation of Bardeen and Townes[8] in which q is the gradient of the electric field at the nucleus. The second term is the cosine coupling between the nuclear magnetic moment and the rotational angular momentum. The third term is the interaction between the nuclear magnetic moment and the external field. The fourth term is the interaction between the molecular rotational magnetic moment and the external field.

For the analysis of the present experimental results, it is not necessary to consider the terms in the Hamiltonian which describes the interaction of the other nucleus with J. The most probable value of J is in the neighborhood of 50 and the energy levels of the entire system are described, to a very exact degree of approximation, as the sum of the energies obtained by considering the interaction of each nucleus separately with the molecular rotation. The neglection of the interaction of the second nucleus with J can be formally justified by the procedure discussed by Bardeen and Townes[8] when the quadrupole interaction of the second nucleus is small compared to that of the first nucleus.

Consider the case in which the interaction with the external field is small compared with the quadrupole interaction energy. This case is best represented in the F, m_F representation. F is the total angular momentum of the molecule and m_F is its projection along the direction of the external field. In this representation the first and second terms are diagonal. The matrix elements are given by Condon and Shortley:[9]

$$(J+\tfrac{1}{2}, m_F|\mathcal{H}|J+\tfrac{1}{2}, m_F)=eqQ[1+3/(2J+3)]/8 +\tfrac{1}{2}cJ+g_J\mu_0 Hm_F+(g_I-g_J)\mu_0 Hm_F/2F, \quad (2a)$$

$$(J-\tfrac{1}{2}, m_F|\mathcal{H}|J-\tfrac{1}{2}, m_F)=eqQ[1-3/(2J-1)]/8 -\tfrac{1}{2}cJ+g_J\mu_0 Hm_F-(g_I-g_J)\mu_0 Hm_F/2F, \quad (2b)$$

$$(J\pm\tfrac{1}{2}, m_F|\mathcal{H}|J\mp\tfrac{1}{2}, m_F) =(g_I-g_J)\mu_0 H[1-(m_F/F)^2]^{1/2}. \quad (2c)$$

Since the states $J\pm\frac{3}{2}$ are separated from the $J\pm\frac{1}{2}$ states by an energy difference large compared with the energy difference between $J+\frac{1}{2}$ and $J-\frac{1}{2}$ at weak fields, the four by four matrix will approximately factor. If the two by two matrix involving the $J\pm\frac{1}{2}$ states is diagonalized the following is obtained, without any further approximations:

$$\begin{aligned}E(J\pm\tfrac{1}{2})=&\tfrac{1}{2}[b(2+\alpha-\beta)+2g_J\mu_0 Hm_F]\\ &\pm\tfrac{1}{2}[b^2(2+\alpha-\beta)^2-4b^2(1+\alpha)(1-\beta)\\ &+2b(\alpha+\beta)(kz+cJ)+4k^2(1-3z^2/4)\\ &+2kcJz+c^2J^2]^{\frac{1}{2}}, \quad (3)\end{aligned}$$

where $\alpha=3/(2J+3)$, $\beta=3/(2J-1)$, $k=(g_I-g_J)\mu_0 H$, $b=eqQ/8$, and $z=m_F/F$. After some simplification and the retention of terms through $1/J$ (3) becomes:

$$E(J\pm\tfrac{1}{2})=b+g_J\mu_0 Hm_F\pm\tfrac{1}{2}[(3b/J+cJ)^2 +2kz(3b/J+cJ)+4k^2(1-3z^2/4)]^{\frac{1}{2}}. \quad (4)$$

The selection rules for the perturbation due to the oscillating magnetic field are $\Delta F=0$, ±1 and $\Delta m_F\pm1$. The frequencies of the components due to the transitions $\Delta F=0$ are zero through terms in $1/J$, except for the term $g_J\mu_0 H$ which is zero at zero field and small at intermediate fields. The moment change in the strong fields in the deflecting magnets would be $g_J\mu_0$ for these transitions and they would not be observable.

The transitions $\Delta F=\pm1$ lead to the following frequencies:

$$\begin{aligned}f=W(J\pm\tfrac{1}{2}, m_F\pm1)-W(J\mp\tfrac{1}{2}, m_F)/h\\ =\pm[f_0^2+2\nu f_0 z+4\nu^2(1-3z^2/4)]^{\frac{1}{2}},\\ f_0=(3b/J+cJ)/h, \quad \nu=k/h,\end{aligned} \quad (5)$$

where both k and ν are negative when g_I is negative, as for all nuclei considered in this paper. The term f_0 may itself be negative. Evidently, only the absolute value of f is of interest. The difference between $m\pm1$ and m has been neglected since it leads, in all cases of interest, to terms which are small compared with the main terms. It is seen at once that f_0 is the frequency of the components of the line at zero field. The expression for f_0 agrees with that of NR.

---

[8] J. Bardeen and C. H. Townes, Phys. Rev. 73, 97 (1948).

[9] E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, Cambridge, 1935), pp. 63, 64, 67. The greatest contribution to the energy occurs through the term in eqQ for all cases of interest here. The matrix elements involving this term are, therefore, exact. Since cJ is of the same order as eqQ/J for the molecules here considered and for rotational states of large population, terms involving c and J to a lesser power than the first are ignored. The interaction energies of the nuclear and rotational magnetic moments with the applied magnetic field are less than the interaction energy of the quadrupole moment with the gradient of the electric field at the nucleus for all magnetic fields here considered. Terms involving g_I and g_J and also F to the order $1/F^2$ are, therefore, ignored.

Equation (5) reduces to:

$$f_H = |2\nu(1-3z^2/4)^{\frac{1}{2}}| \qquad (6)$$

at magnetic fields for which $|2\nu| \gg |f_0|$. Since the values of f_0 reported in the paper do not exceed 160 kc and since 2ν increases at the rate of somewhat more than 2 kc/gauss, the expression (6) gives an adequate representation of the line components at very moderate fields. Expression (5) differs from that of Ramsey[7] in the terms involving the $\mathbf{I}\cdot\mathbf{J}$ interaction constant and g_J.

Consider the zero field line whose components have a frequency $f_0 = (3b/J + cJ)/h$. The line shape, of course, depends on the population of the various J states. The intensity at a particular frequency is determined by the product of the "density function," $|dJ/df|$ and by the population of the J states which contribute to a particular frequency interval. The intensity then is:

$$\mathrm{Int} \propto |dJ/df| J \exp(-\alpha^2 J^2), \qquad (7)$$

where

$$\alpha^2 = h^2/8\pi^2 IkT,$$

in which I is the moment of inertia of the molecule and T the temperature of the oven. Then

$$\mathrm{Int} \propto J^3 \exp(-\alpha^2 J^2)/|cJ^2 - 3b|. \qquad (8)$$

TABLE I. The temperature, internuclear distance, most probable value of J, and α^2 for certain alkali halides.

Molecule	T(°K)	$r_e(A)$	$\alpha^2 \times 10^4$	$\bar{J}$
NaF	1250	2.1	4.58	33
NaCl	1025	2.51	2.65	43
NaBr	1000	2.64	1.92	51
NaI	975	2.90	1.49	58
KBr	1000	2.94	1.05	69

This expression, of course, does not give the intensity in terms of the experimentally observed quantity, f_0, but only in terms of J. If c has the same sign as b it is apparent that a maximum of intensity will occur at $J = (3b/c)^{\frac{1}{2}}$ and that this intensity will occur at the frequency $f_{\min} = (12bc)^{\frac{1}{2}}/h$. At all frequencies other than $f_{\min}$, two values of J contribute to the intensity. These two values are related by $J_1 J_2 = 3b/c$. If $f_{\min}$ occurs at a value of J for which the population is very low, as, for example, when $b \to 0$ or $c \to 0$, the total integrated intensity within the maximum defined by $cJ^2 = 3b$ is very small and an analytic maximum may occur. In the limiting case, $c = 0$, $f_0 = 3b/Jh$ and the maximum intensity occurs at $J = \sqrt{3}\bar{J}$ corresponding to $f = \sqrt{3}b/\bar{J}h$, where $\bar{J}$ is the most probable value of J. When $b = 0$, $f_0 = cJ/h$ and the maximum intensity occurs at $J = \bar{J}$ and $f = c\bar{J}/h$. The general condition which determines the analytic maximum is found by differentiation of (8) with respect to f.

$$J^2 = \{6\alpha^2 b + c \pm [(6\alpha^2 b + c)^2 - 72\alpha^2 bc]^{\frac{1}{2}}\}/4\alpha^2 c. \qquad (9)$$

Since J^2 must be real and positive the condition that must be fulfilled for the occurrence of an analytic maximum for the intensity as a function of J is that $(6\alpha^2 b + c)^2 \geqslant 72\alpha^2 bc$. From a study of this inequality the following conclusions can be drawn.

TABLE II. Magnitude and sign of eqQ/h and c/h. The columns A, B, and C refer, respectively, to the reference for the magnitude of eqQ/h, the sign of eqQ/h, and the magnitude of c/h. Where no reference is given the results are from the present work. The symbols HF and ZF refer to results at high field and zero field of the magnetic resonance method. The symbol ER refers to results of the electric resonance method.

Molecule	Resonance	$8b/h$ eqQ/h (Mc)	A	B	c/h (kc)	C
NaF	Na^{23}HF	−8.12	13	13		
	ZF	−8.40	5		1	5
NaCl	Na^{23}ZF	−5.67			0.37	
	HF	−5.40	1	13		
	ZF	−5.608	5		1	5
NaBr	Na^{23}HF	−4.68	1	13		
	ZF	−4.88			0.67	
NaI	Na^{23}HF	−3.88	1	13		
	ZF	−3.96			0.69	
KBr	Br^{79}ER		15		$\leqslant 2$	15
	$v=0$	+10.24				
	$v=1$	+11.22				
	$v=2$	+12.20				
	Br^{81}ER					
	$v=0$	+8.553			$\leqslant 2$	

1. If $0.01685 < b\alpha^2/c < 1.65$ there is only one maximum, determined by $J = (3b/c)^{\frac{1}{2}}$.

2. If $b\alpha^2/c = 0.01685$ or 1.65 two maxima exist, but they coincide.

3. For values of b, c, and α not satisfying 1 and 2, two maxima occur, one for $J = (3b/c)^{\frac{1}{2}}$ and the other for the value of J determined by the root of (9).

When two maxima of intensity occur, two values of J contribute to the intensity at any frequency. We have, in the preceeding analysis, neglected one of these values; however, the maximum is not much affected, since one set of J values, of very low population, gives a monotonically varying intensity while the other, of higher population gives rise to the maximum.

When c has a sign opposite to that of b, there is a single maximum of intensity for a value of J given by (9). The sign to be taken is that which makes J positive. The value of $(3b/J + cJ)/h$ may take on both positive and negative values. Evidently, since the absolute value of f is observed, the addition of the intensity arising for a negative f and a positive f may seriously modify the position of the intensity maximum as determined from (9).

In Table I are given the values of the quantities α^2 and $\bar{J}$ appropriate to the molecules studied in this work. The temperatures of the ovens from which the molecules were evaporated are also given in the table. The internuclear distances of all the molecules except NaF are obtained[10] from electron diffraction data while that of NaF is estimated by Wick.[11] In Table II are given values of the quadrupole and dipole interaction

---

[10] Maxwell, Hendricks, and Mosley, Phys. Rev. **52**, 968 (1937).

[11] G. C. Wick, Phys. Rev. **73**, 51 (1948).

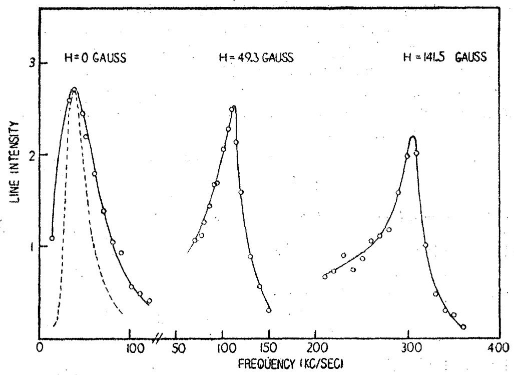

FIG. 1. Nuclear resonance spectra, $(J+\frac{1}{2})\leftrightarrow(J-\frac{1}{2})$, of Na^{23} in NaCl at several magnetic fields. The dotted curve is a theoretical curve using the values: $b/h=-709$ kc and $c/h=-0.16$ kc.

constants obtained from observations on various kinds of spectra with the exception of the spectrum arising from the transition $(J+\frac{1}{2})\leftrightarrow(J-\frac{1}{2})$ here considered. The data include the results of the present observations on the transitions $(J\pm\frac{3}{2})\leftrightarrow(J\pm\frac{1}{2})$. It is evident from a calculation involving the data of Tables I and II that an analytic maximum in the intensity distribution for the line $(J+\frac{1}{2})\leftrightarrow(J-\frac{1}{2})$ cannot occur in any of the resonances here observed if b/h and c/h have the same sign and for a considerable range of c/h around that given in Table II.

APPARATUS AND METHOD

The apparatus is the same as that used in previous experiments on molecular beams. The relevant characteristics of the apparatus are described in earlier papers.[12,13] The only modification was the addition of a re-entrant cavity, mounted on a flexible bellows. The cavity could be inserted into the gap of the C magnet, immediately adjacent to the hairpin which produced the rf field. The magnetic field could then be measured during the course of a run by use of a conventional flipcoil. The flipcoil was used during most of the experiments to measure the fields and was always used to determine the zero field condition. In several experiments a double oven mount previously described[14] was used and the field was calibrated by use of the Li^7 resonance in LiCl. The F^{19} resonance in NaF was used for this purpose when the Na^{23} resonance in this molecule was studied.

EXPERIMENTAL DATA

A. NaCl

Figure 1 shows the observed $(J+\frac{1}{2})\leftrightarrow(J-\frac{1}{2})$ line due to the sodium nucleus in NaCl at fields which vary from zero to one sufficiently high so that the frequency of the maximum and the line shape are only trivially affected by terms containing b and c. Of particular interest is the frequency of the maximum at zero field, $f_0=37$ kc, whose width at half-intensity is 54 kc.

Figure 2 shows the $(J\pm\frac{3}{2})\leftrightarrow(J\pm\frac{1}{2})$ line due to the sodium nucleus in NaCl at zero field. The present data shows more structure for this resonance than was previously observed by NR and by Zeiger and Bolef.[5]

The $(J\pm\frac{3}{2})\leftrightarrow(J\pm\frac{1}{2})$ line, in the absence of $\mathbf{I}\cdot\mathbf{J}$ interaction and any variation of b with J and v should occur at a frequency $f=2b/h$. The addition of the $\mathbf{I}\cdot\mathbf{J}$ interaction splits the line giving a doublet of separation $2c\bar{J}/h$, symmetrical about the frequency $2b/h$.

Zeiger and Bolef observed only the splitting, indicated by dd in Fig. 2, and attributed this to the $\mathbf{I}\cdot\mathbf{J}$ interaction. The value of ~ 1 kc is given for c/h. If the $\mathbf{I}\cdot\mathbf{J}$ splitting is assumed to give rise to the two maxima (dd in Fig. 2) the results of the present experiment give the same value for the separation $2c\bar{J}/h$, but the additional structure complicates the interpretation of the curve. It is equally possible to assume that the two maxima d', d', in Fig. 2 correspond to the $\mathbf{I}\cdot\mathbf{J}$ splitting and that the approximate repetition of the pattern corresponds to a marked variation of b with v. In fact, if we follow the notation of Zeiger and Bolef the observed curve can be fitted quite satisfactorily by the following constants:

$$b/h=-709\text{ kc},\quad |c\bar{J}/h|=16\text{ kc},\quad \bar{J}=43,\quad \gamma=0.25,$$
$$|c/h|=0.37\text{ kc},\quad P=+85\text{ kc},$$

where $\gamma=eq^{(J)}Q/2\sqrt{2}\alpha c$, $P=eq^{(v)}Q/4h$, and $q=q^{(v)}+q^{(J)}J(J+1)+q^{(v)}(v+\frac{1}{2})$. The sign of b/h is obtained from the measurements of Logan, Coté, and Kusch,[13] and cannot be determined from an analysis of the line $(J\pm\frac{3}{2})\leftrightarrow(J\pm\frac{1}{2})$. The sign of c/h cannot be determined from an analysis of this line but can be inferred from the position of the line $(J+\frac{1}{2})\leftrightarrow(J-\frac{1}{2})$. It is evident from a comparison of the observed curve with that calculated that a better fit could be obtained by considering in addition to the variation of q with J and v a marked decrease of the quantity c/h with vibrational

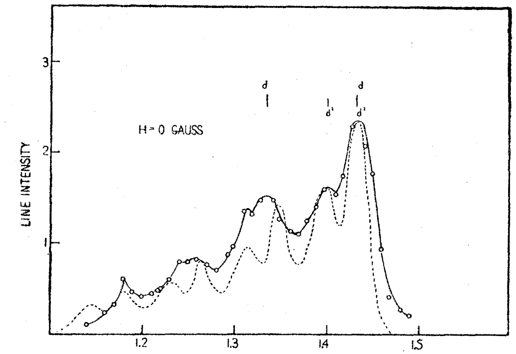

FIG. 2. Nuclear resonance spectrum of Na^{23} in NaCl arising from transitions $(J\pm\frac{3}{2})\leftrightarrow(J\pm\frac{1}{2})$. The dotted curve is a theoretical curve calculated from the following values: $b/h=-709$ kc, $c\bar{J}/h=16$ kc, $\bar{J}=43$, $\gamma=0.25$, $P=+85$ kc, and $c/h=0.37$ kc.

---

[12] H. Taub and P. Kusch, Phys. Rev. **75**, 1481 (1949).

[13] Logan, Coté, and Kusch, Phys. Rev. **86**, 280 (1952).

[14] P. Kusch and H. M. Foley, Phys. Rev. **74**, 250 (1948).

quantum number. As will be shown, the present interpretation yields a value of c more nearly in accord with that required to interpret the $(J+\frac{1}{2})\leftrightarrow(J-\frac{1}{2})$ line than does that of Zeiger and Bolef.

The $(J+\frac{1}{2})\leftrightarrow(J-\frac{1}{2})$ line shows shapes which are qualitatively the same as those which would be expected on the basis of the earlier discussion, both in the presence of an external field and at zero field.

At zero field where the line shape and position is sensitive to the values of b and c, it is necessary to consider both possible signs of c, since the sign is previously undetermined. From the analysis of Zeiger and Bolef and assuming a negative sign for c, $c/h=-1.0$ kc, and $f_0=92$ kc. If the present analysis of the spectrum arising from $(J\pm\frac{3}{2})\leftrightarrow(J\pm\frac{1}{2})$ is used and a negative sign is assumed for c, $c/h=-0.37$ kc and $f_0=56$ kc. In order to obtain the observed value of $f_0=37$ kc it is necessary that $c/h=-0.16$ kc.

The theoretical line shape has been calculated assuming a value of $c=-0.16$ kc and appears as the dotted curve in Fig. 1. To avoid the infinities which occur in Eq. (8), $|dJ/df|$ has been read, for a finite interval df, from a graph in which f is plotted as a function of J. These quantities when multiplied by the Boltzmann function give the intensity distribution, uncorrected for the resolution properties of the apparatus.

This uncorrected curve has been modified by a numerical integration over the usual resonance function where a resolution half-width of 5 kc has been assumed. The intensity has been adjusted to give coincidence of the peaks at the maximum. The general features of the calculated and observed curves are similar, though the observed width at half-intensity, 54 kc is considerably greater than the calculated width of 28 kc.

It is instructive to examine the case when c is positive. In Fig. 3 the intensity as calculated from Eq. (8) for $b/h=-709$ kc and several values of c, is plotted as a function of f in the dotted curves. The solid curves indicate the intensity as summed for positive and negative f. No resolution function has been applied since the structures are broad as compared to the resolution half-width. It is evident that no positive value of c will give a resonance curve of the appropriate width and at the appropriate frequency. The curve for $c=0$ has a shape similar to the observed shape. The maximum occurs at about 28 kc and the width is 32 kc, still less than the observed width. It is evident that a small positive value of c will further reduce the calculated value of f_0 and increase the calculated width.

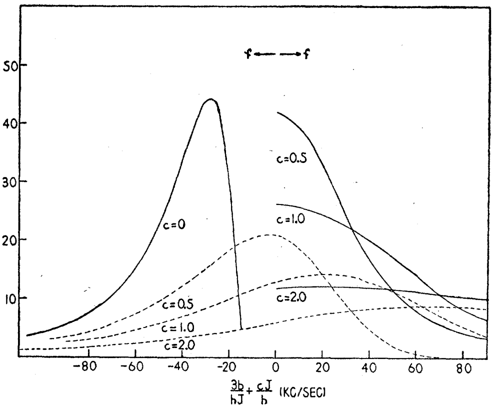

FIG. 3. Calculated line shapes for the $(J+\frac{1}{2})\leftrightarrow(J-\frac{1}{2})$ line of Na^{23} in NaCl for several positive values of c using $b/h=-709$ kc. The solid curves indicate the intensity as summed for positive and negative f.

It is probable that the more satisfactory explanation of the zero field line occurs for an analysis which gives the experimentally observed position of the line rather than the experimentally observed width for the line. Several factors will serve to increase the line width from that here calculated; among these are a variation of b with both J and v and a possible variation of c with J and v. In view of the uncertainties which occur in other analyses which purport to determine the magnitude of c/h, it might appear that a value, of at least as great a validity as previous ones, is $c/h=-0.16$ kc. However, since equally serious inconsistencies arise in the cases of other molecules where the interpretation of the $(J\pm\frac{3}{2})\leftrightarrow(J\pm\frac{1}{2})$ resonance is not ambiguous, it cannot be asserted that $c/h=-0.16$ kc for Na in NaCl.

A little analysis shows that the variation of b with J and v as given by our analysis of the line $(J\pm\frac{3}{2})\leftrightarrow(J\pm\frac{1}{2})$ will not significantly shift the line maximum. It is, however, possible to assume a variation of c with J which would shift the maximum rather considerably. If this variation were of such a nature that, for J states of high population, the Hamiltonian of the interaction is of the form $c'\mathbf{I}\cdot\mathbf{J}/J$, the observed splitting in the $(J\pm\frac{3}{2})\leftrightarrow(J\pm\frac{1}{2})$ line is $2c'$. The zero field line, $(J+\frac{1}{2})\leftrightarrow(J-\frac{1}{2})$ then has the frequency $f_0=(3b/J+c')/h$. From an analysis of the line $(J\pm\frac{3}{2})\leftrightarrow(J\pm\frac{1}{2})$, $|c'|=16$ kc. The intensity distribution is exactly as shown for the case $c=0$ in Fig. 3 except that the frequency scale is shifted. If $c'=-16$ kc, the maximum occurs at 44 kc. While no other evidence exists to indicate the validity of the analysis it is apparent that a detailed fit of experimental data to a calculated position cannot be made without further knowledge of the variation of c with J and v.

Figure 4 shows the frequency variation of the resonance as a function of magnetic field. The line whose slope is $2g(Na^{23})\mu_0/h$ is drawn for reference. The good agreement justifies the assumption that the resonance is due to the sodium nucleus and indicates that the line is, indeed, the spectroscopic structure which the theory has assumed.

B. NaBr

The lines observed in NaBr and attributed to the $(J+\frac{1}{2})\leftrightarrow(J-\frac{1}{2})$ transition of Na are similar to those observed in NaCl except at zero field. No maximum was observed for this resonance at zero field. It is to be

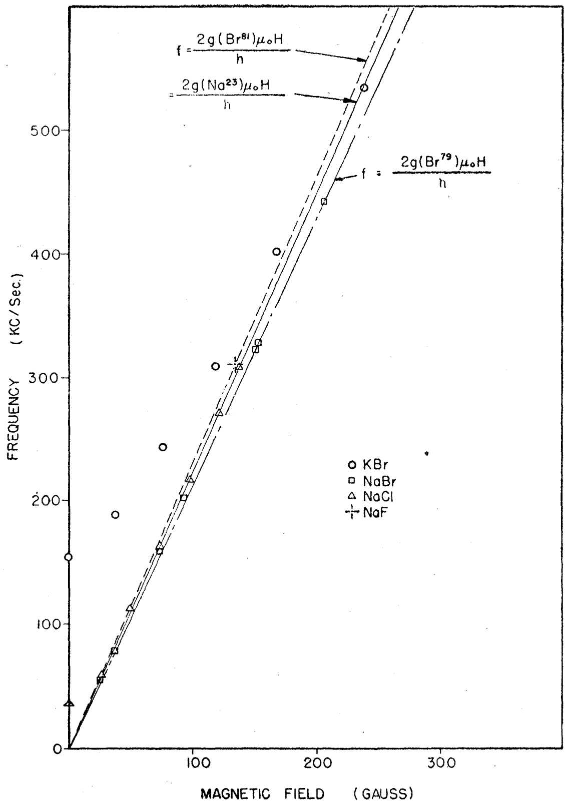

FIG. 4. The experimental data which show the variation of the intensity maximum with magnetic field for the Na^{23} resonance in NaCl, NaBr, and NaF and for the Br^{79} and Br^{81} resonances in KBr. The lines whose slopes are $2g(Br^{79})\mu_0$, $2g(Br^{81})\mu_0$ and $2g(Na^{23})\mu_0$ are shown for reference.

noted that the lines when measured at fields sufficiently greater than zero to bring them into a manageable range of frequency were sharp. For example, when the resonance maximum occurred at 52 kc, the curve had a width of 26 kc.

The g_I's of the component nuclei, Na^{23}, Br^{79}, Br^{81}, are so nearly the same that the error in field measurement precludes an identification of the nucleus responsible for the observed resonances by a measurement of the slope of the frequency *versus* field curve. However, the line does not show a splitting at fields for which a splitting greater than the observed line width should occur if the bromine nuclei are responsible for the resonance. Hence the resonance is unambiguously ascribed to the sodium nucleus.

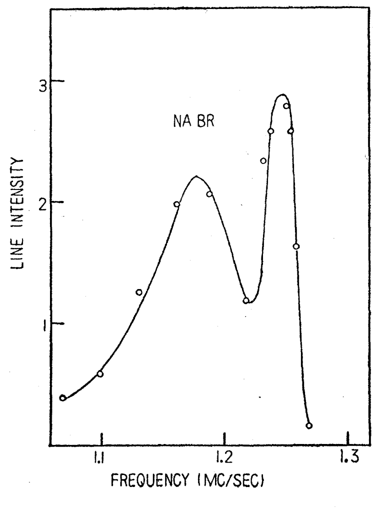

FIG. 5. Nuclear resonance spectrum of Na in NaBr arising from transitions $(J\pm\frac{3}{2})\leftrightarrow(J\pm\frac{1}{2})$ at zero field.

The $(J\pm\frac{3}{2})\leftrightarrow(J\pm\frac{1}{2})$ lines of Na in NaBr are shown in Fig. 5. The lines are identified with Na since the quadrupole interaction determined from these lines is in substantial agreement with that derived from high field data where the assignment of the structure to Na is unambiguous. The splitting shown in Fig. 5 has not previously been observed. Values of $eqQ/h=-4.88$ Mc/sec ($b=-610$ kc) and $c/h=0.67$ kc/sec are obtained from this curve on the assumption that the splitting is due to the $\mathbf{I}\cdot\mathbf{J}$ interaction. The sign of b is obtained from other evidence.[13] If c is negative, the line $(J+\frac{1}{2})\leftrightarrow(J-\frac{1}{2})$ is sharp and is expected to occur at 70 kc. If c is positive, however, the maximum occurs at about 18 kc if both positive and negative frequencies are considered. When the intensities associated with equal positive and negative frequencies are added, a single broad maximum, decreasing in intensity from zero frequency, is predicted. Neither calculation fits the observed data; the first because the line is in the wrong position and the second because the calculated line width is excessive.

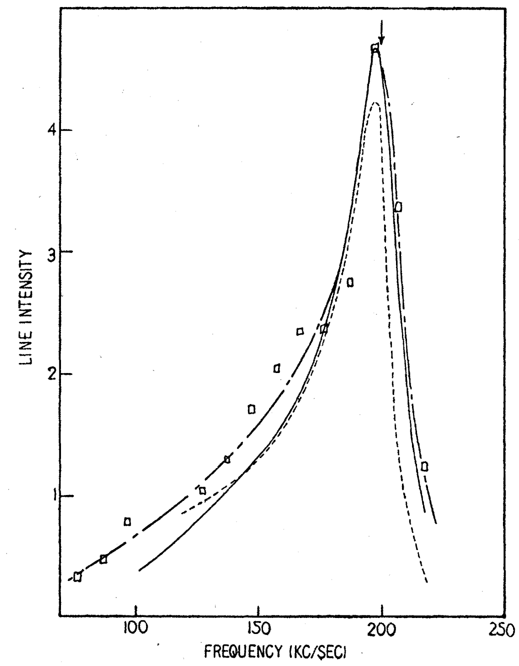

FIG. 6. Nuclear resonance spectrum of Na in NaBr arising from transitions $(J+\frac{1}{2})\leftrightarrow(J-\frac{1}{2})$ at 178 gauss. The dashed curve is the observed curve. The solid curve is a theoretical curve using the values: $b/h=-585$ kc and $c/h=0.67$ kc. The dotted curve is calculated from $f=2\nu(1-3z^2/4)^{\frac{1}{2}}$.

In spite of the difficulties which occur in the analysis of the lines $(J+\frac{1}{2})\leftrightarrow(J-\frac{1}{2})$, at zero field, excellent agreement between the experimentally observed resonance and that calculated is obtained for the observation at "high" field where $2\nu \gg f_0$. The dashed curve in Fig. 6 is the resonance curve of Na in NaBr at a field of 178 gauss. The curve drawn as a solid line is calculated under the assumption that $b/h=-585$ kc and $c/h=+0.67$ kc. Figure 6 is the result of numerical integration. The frequencies as obtained from (5) are plotted as a function of z for several values of J. Values of dz/df are taken from the curves for each J and multiplied by the Boltzmann function to give a quantity proportional to the intensity. The transition probability is very nearly a constant and its variation is ignored. The usual resolution function for a half-width of 5 kc has been applied to give the final intensities in Fig. 6.

The dotted curve shows the intensity distribution at the same field when the high field expression (6) is used. The two curves show that the effect of the constants b and c on the shape and position of the line is very small. The small shift of the maximum in Fig. 6 from $2g_I\mu_0H/h$ arises from the resolution effects in a highly unsymmetrical line. The agreement between the observed and calculated curves is satisfactory and indicates the general validity of the analysis of the line at high field. The resonance has been observed at fields as high as 1400 gauss where it has lost its characteristic shape and is very broad. The characteristic shape is still evident at a field of 500 gauss ($f\sim 1090$ kc) where the width is 170 kc.

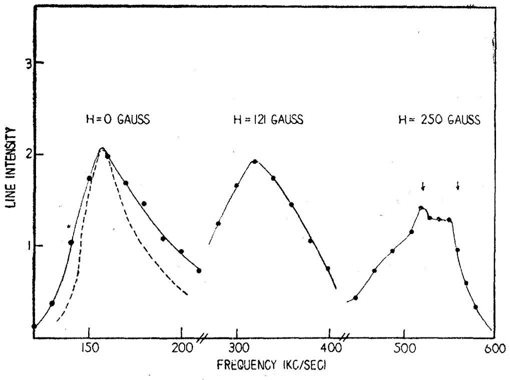

FIG. 7. Nuclear resonance spectra, $(J+\frac{1}{2})\leftrightarrow(J-\frac{1}{2})$, of Br^{79} and Br^{81} in NaBr at several magnetic fields. The dotted curve is a theoretical curve using the values: $b(79)/h=+1670$ kc, $b(81)/h=+1400$ kc, $c(79)/h=+1.21$ kc and $c(81)/h=+1.30$ kc.

The term in g_J has been neglected in all the calculations. To the precision with which the field was measured, g_J is, indeed, negligible.

C. KBr

Typical resonance curves for the line $(J+\frac{1}{2})\leftrightarrow(J-\frac{1}{2})$ for Br^{79} and Br^{81} in KBr are shown in Fig. 7. The splitting due to the two isotopes begins to be apparent in the line of highest frequency. The arrows indicate the frequencies $2g_{79}\mu_0H/h$ and $2g_{81}\mu_0H/h$. Both the splitting and the frequency of the line at sufficiently high fields attribute the line, unambiguously, to the Br isotopes rather than K.

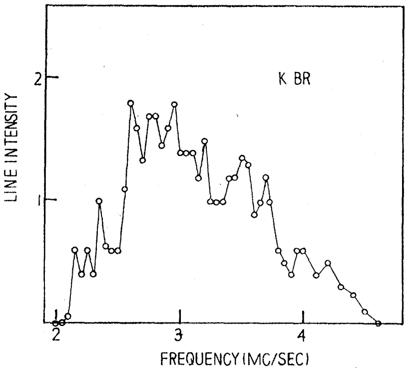

FIG. 8. Nuclear resonance spectrum of Br^{79} and Br^{81} in KBr arising from transitions $(J\pm\frac{3}{2})\leftrightarrow(J\pm\frac{1}{2})$ at zero field.

A resonance curve (Fig. 8) has been observed in KBr with a frequency around 3 Mc. Recent experiments by Fabricand, Carlson, and Lee[15] have produced the data of Table II on the quadrupole interaction of Br in KBr. The quadrupole interaction shows a large change with vibrational state and it should be noted that it is low with respect to any values which might be ascribed to the eqQ's on the basis of Fig. 8. It must be realized, however, that the results of the electrical resonance method are for the $J=0$ state while the most probable J for the present experiment is about 70. A meaningful analysis of the bromine resonance in Fig. 8 appears to be impossible.

The ratio of the quadrupole moments of the bromine isotopes is known[16] to be $Q_{79}/Q_{81}=1.194$ and the ratio of the g_I values[17] to be $g_{81}/g_{79}=1.078$.

To satisfy the known ratios of the b's and c's, to describe approximately the resonance of Fig. 8, and to give a good fit to the data on the $(J+\frac{1}{2})\leftrightarrow(J-\frac{1}{2})$ line at zero field, the following constants have been found: $c_{79}/h=+1.21$ kc, $c_{81}/h=+1.30$ kc, $b_{79}/h=+1670$ kc, $b_{81}/h=+1400$ kc.

The dotted curve shown for zero field in Fig. 7 indicates an agreement in the frequency of the maximum and the shape of the line. The excessive width of the observed line is not unexpected in view of the large variation of b with J and v. In view of the inconsistencies which arise for the case of the Na resonances $(J\pm\frac{3}{2})\leftrightarrow(J\pm\frac{1}{2})$ and $(J+\frac{1}{2})\leftrightarrow(J-\frac{1}{2})$, the given b's and c's are not to be construed as highly meaningful quantities.

D. NaF

The $(J+\frac{1}{2})\leftrightarrow(J-\frac{1}{2})$ resonance due to Na^{23} in NaF was identified by its frequency at a fixed value of magnetic field. The line had the same general shape as

---

[15] Fabricand, Carlson, and Lee (private communication).

[16] C. H. Townes, J. Chem. Phys. **17**, 782 (1949).

[17] J. R. Zimmerman and D. Williams, Phys. Rev. **76**, 350 (1949).

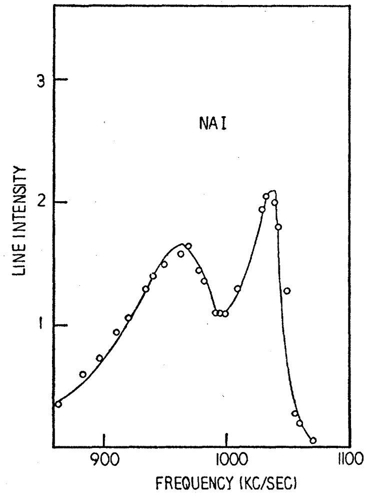

FIG. 9. Nuclear resonance spectrum of Na^{23} in NaI arising from transitions $(J\pm\frac{3}{2})\leftrightarrow(J\pm\frac{1}{2})$ at zero field.

that of the lines previously discussed. Unfortunately, the zero field $(J+\frac{1}{2})\leftrightarrow(J-\frac{1}{2})$ line was obscured by a very broad F^{19} resonance.

E. NaI

The $(J\pm\frac{3}{2})\leftrightarrow(J\pm\frac{1}{2})$ resonance of Na in NaI at zero field is shown in Fig. 9. The resonance, unresolved into two components, has been observed[1] previously. From this resonance it is found that $eqQ/h=-3.96$ Mc/sec, where the negative sign is known from other evidence,[13] and that $|c/h|=0.69$ kc. A line has been observed at zero field and attributed to the $(J+\frac{1}{2})\leftrightarrow(J-\frac{1}{2})$ resonance of Na by an observation of the frequency of this line at fields where $2\nu\gg f_0$. The line has the characteristic shape observed for Na in NaCl and for Br in KBr, i.e., a drop in intensity on the low frequency side of the maximum and a slower drop in intensity on the high frequency side. This appearance is characteristic of a c of the same sign as b when c is not extremely small. The observed value of f_0 is 36 kc which then leads to a c of -0.23 kc. The observed width is 50 kc. The discrepancy between the data obtained from the two zero field resonances is notable. In all cases the value of c obtained from the $(J+\frac{1}{2})\leftrightarrow(J-\frac{1}{2})$ line is less than that obtained from the $(J\pm\frac{3}{2})\leftrightarrow(J\pm\frac{1}{2})$ line.

DISCUSSION

In each of the diatomic molecules which has been studied except NaF, a single resonance, attributable to the transition $(J+\frac{1}{2})\leftrightarrow(J-\frac{1}{2})$ has been observed. For the Cl nucleus in NaCl and especially for the K nucleus in KBr, the nuclear g value is so small that a transition results in a small moment change and hence leads to a resonance of low intensity. A careful search under optimum experimental conditions might yield a resonance of Cl in NaCl. No resonance due to Br or I in the sodium halides has been observed in any of the several kinds of spectra observed by molecular beams methods. It may be assumed that the internal interactions, principally the quadrupole interaction, are very large and that the spectrum, therefore, is so broad that the intensity at any frequency is very small. Large internal interactions would also prevent the observation of the $(J+\frac{1}{2})\leftrightarrow(J-\frac{1}{2})$ lines for Br and I in NaBr and NaI. It is interesting to note that in the case of NaF, where the nuclear moments of both nuclei are fairly large and where the internal interactions are not large, resonances have been observed for both Na and F, even though they cannot be analyzed separately.

Several lines of evidence have been developed on the internal interactions of the alkali halides. The electrical resonance method gives unambiguous results but only for states with a very low J value. The magnetic resonance method at high magnetic field gives the quadrupole interaction energy for a statistical distribution in J as does a measurement of the transition $(J\pm\frac{3}{2})\leftrightarrow(J\pm\frac{1}{2})$ at zero field. The results of the magnetic resonance method at high and low fields are in excellent agreement and may, therefore, be assumed to give a reliable value of the quadrupole interaction energy. The line $(J\pm\frac{3}{2})\leftrightarrow(J\pm\frac{1}{2})$ gives, as well, a value for the internal dipole interaction for the most probable value of J. Finally, the line $(J+\frac{1}{2})\leftrightarrow(J-\frac{1}{2})$ at zero field gives a frequency dependent on both the quadrupole and dipole interaction energies. On the assumption that the quadrupole interaction constant is correctly determined by other lines of evidence, the value of c/h as determined from the $(J+\frac{1}{2})\leftrightarrow(J-\frac{1}{2})$ line on the basis of present theory is in marked disagreement with that determined from the $(J\pm\frac{3}{2})\leftrightarrow(J\pm\frac{1}{2})$ line. A satisfactory explanation of the discrepancy may require a more refined theoretical treatment, the inclusion of additional interaction terms and a knowledge of the variation with J and v of terms here assumed to be constant.

We wish to express our thanks to Mr. Ralph Logan and Mr. Stefan Ochs for assistance in the experimental work. Professor H. M. Foley has given much assistance in the theoretical interpretation of the results.