# The Radiofrequency Spectrum of $Rb^{85}F$ and $Rb^{87}F$ by the Electric Resonance Method*

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(Received February 24, 1950)

The radiofrequency spectrum of the two molecular species $Rb^{85}F$ and $Rb^{87}F$ was studied by the molecular beam electric resonance method. The electrical quadrupole interaction constant, $eq_1Q_1/h$, of Rb in RbF was determined for $Rb^{87}F$ in rotational states $J=1$ and $J=2$ for the first few vibrational states, and for $Rb^{85}F$ in rotational state $J=1$ for the first few vibrational states. The interaction constants are unusually large for an alkali halide molecule; for the zeroth vibrational state of $Rb^{85}F$, $eq_1Q_1/h=-70.31\pm0.10$ Mc/sec. and for the zeroth vibrational state of $Rb^{87}F$, $eq_1Q_1/h=-34.00\pm0.06$ Mc/sec. The absolute value of the interaction constant decreases about 1.1 percent from one vibrational state to the next higher one; the values of the interaction constants for rotational states $J=1$ and $J=2$ are the same within the limit of error. The ratio of the electric quadrupole moment of $Rb^{85}$ to that of $Rb^{87}$ is $+2.07\pm0.01$.

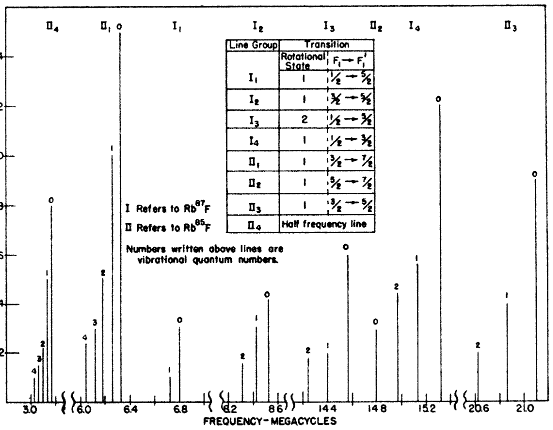
Results are reported on the spin-orbit coupling $c_2(\mathbf{I}_2\cdot\mathbf{J})$, between the spin of the fluorine nucleus and the molecular rotational angular momentum. For the zeroth vibrational state of $Rb^{85}F$, $|c_2/h|=11\pm3$ kc/sec. and for the zeroth vibrational state of $Rb^{87}F$, $|c_2/h|=14\pm4$ kc/sec. No variation in $|c_2/h|$, with vibrational state was observed.

Finally, an unpredicted line group was observed in the spectrum at one-half the frequency of one of the line groups in the $Rb^{85}F$ spectrum. Possible origins of this line group are discussed, including that of a double quantum transition.

The vibrational frequency, $\omega_0$, of $Rb^{85}F$ is $340\pm68$ $cm^{-1}$.

## I. INTRODUCTION

THE radiofrequency spectrum of the two isotopic species of RbF—$Rb^{87}F$ and $Rb^{85}F$—have been studied by the molecular beam electric resonance method.[1,2] This technique permits the study of the energy levels in a static electric field of polar diatomic molecules which are in the $^1\Sigma$ electronic state, in a low vibrational state, and in the rotational state $J=1$. Sometimes molecules in the rotational state $J=2$ can also be studied. The research reported in this paper is a continuation of the studies of the internal interactions of the alkali fluoride molecules.[2,3] The apparatus used was the one described in references 1 and 2, and further details on the experimental technique are given in reference 3.



| Line Group | Transition | |
|---|---|---|
| | Rotational State | $F_1\rightarrow F_1'$ |
| I₁ | 1 | $\frac{1}{2}\rightarrow\frac{5}{2}$ |
| I₂ | 1 | $\frac{3}{2}\rightarrow\frac{5}{2}$ |
| I₃ | 2 | $\frac{1}{2}\rightarrow\frac{3}{2}$ |
| I₄ | 1 | $\frac{1}{2}\rightarrow\frac{3}{2}$ |
| II₁ | 1 | $\frac{3}{2}\rightarrow\frac{7}{2}$ |
| II₂ | 1 | $\frac{5}{2}\rightarrow\frac{7}{2}$ |
| II₃ | 1 | $\frac{3}{2}\rightarrow\frac{5}{2}$ |
| II₄ | Half frequency line | |

FIG. 1. Spectrum observed for $Rb^{85}F$ and $Rb^{87}F$ under low electric field conditions (i.e., $\mu^2E^2/\hbar^2/2A\ll|eq_1Q_1|$). Change in beam intensity is expressed in cm of deflection on a galvanometer scale. All the lines were not taken under comparable conditions so line intensities cannot be compared indiscriminately. Fine structure of the lines is not indicated.

Under low field conditions the frequencies of the transitions induced are determined primarily by the internal molecular interactions. The largest of these is the electrical quadrupole interaction associated with the Rb nucleus, and it was determined for each molecular species for several vibrational states. The interaction constants for the RbF molecules are very much larger than those for $CsF$[2] or $K^{39}F$[3] or, indeed, than those for any other alkali halide molecule yet studied.

A splitting of the spectral lines of both $Rb^{87}F$ and $Rb^{85}F$ was observed. This is caused primarily by a spin-orbit interaction between the fluorine nucleus and the molecular rotational angular momentum. The magnetic dipole-dipole interaction between the two nuclei also contributes slightly to this splitting.

The appearance of an unpredicted line group at exactly one-half the frequency of a line group in the weak field spectrum of $Rb^{85}F$ is reported. Possible explanations for these lines are discussed, including the one that they are double quantum transitions in which two one-half frequency quanta provide the energy for the transitions. However, none of these explanations seems to account for all the observations.

## II. EXPERIMENTAL DATA

The spectra for the two isotopic species $Rb^{87}F$ and $Rb^{85}F$, were observed simultaneously[4] under conditions of low electric field intensity, i.e., the interaction energy of the external electric field with the molecule was small compared to the electrical quadrupole interaction energy associated with the Rb nucleus. The spectrum (see Fig. 1) consists of some 26 lines occurring in the

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* This research has been supported in part by the ONR.

** Submitted by Vernon Hughes in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physics at Columbia University.

[1] H. K. Hughes, Phys. Rev. **72**, 614 (1947).

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

[3] L. Grabner and V. Hughes (to be published).

[4] Simultaneous observation of the spectra of both isotopic species was possible because the $A$ and $B$ field voltages which refocus one molecular isotope refocus the other molecular isotope as well. All the data were taken using the $(1,\pm1)_A-(1,0)_B$ refocused beam as described in reference 3.

frequency range from about 3 Mc/sec. to 21 Mc/sec.; a search was made over the more extended range from 1 Mc/sec. to 45 Mc/sec. but no lines were found other than those shown. These lines are analyzed into line groups which are designated by Roman numerals with subscripts. The lines within a group correspond to the same transition for different vibrational states, and they are distinguished by the vibrational quantum numbers which are written directly above the lines. It will be shown that with the exception of the line group near 3 Mc/sec., the spectrum can be understood as due to transitions of molecules with rotational states $J=1$ and $J=2$.

## III. THEORY

The following Hamiltonian is assumed for the diatomic molecule in a static electric field.[2]

$$\mathcal{H}=\frac{\hbar^2}{2A}\mathbf{J}^2-\boldsymbol{\mu}\cdot\mathbf{E}-\frac{eq_1Q_1}{2I_1(2I_1-1)(2J-1)(2J+3)}\times\{3(\mathbf{I}_1\cdot\mathbf{J})^2+\tfrac{3}{2}(\mathbf{I}_1\cdot\mathbf{J})-\mathbf{I}_1^2\mathbf{J}^2\}+c_2(\mathbf{I}_2\cdot\mathbf{J})+\frac{g_1g_2\mu_N^2}{r^3}\left\{\mathbf{I}_1\cdot\mathbf{I}_2-3\frac{(\mathbf{I}_1\cdot\mathbf{r})(\mathbf{I}_2\cdot\mathbf{r})}{r^2}\right\}. \quad (1)$$

The first term in which $\mathbf{J}$ is the rotational angular momentum and $A$ is the moment of inertia is the rotational energy term. The second term gives the interaction of the external electric field $\mathbf{E}$ with the permanent electric dipole moment $\boldsymbol{\mu}$ of the molecule. The third term is the electrical quadrupole interaction between the electric quadrupole moment of the Rb nucleus, $Q_1$, and a second derivative of the electric potential at the position of the Rb nucleus, $q_1$, produced by those charges in the molecule which are exterior to the nucleus.[5] (The subscript $_1$ refers to the Rb nucleus.) $\mathbf{I}_1$ is the spin of the Rb nucleus. There is no electrical quadrupole interaction with the F nucleus because its spin is $\frac{1}{2}$. The fourth term is a cosine coupling between the spin of F designated by $\mathbf{I}_2$ and the rotational angular momentum of the molecule.[6, 7] The last term is the magnetic dipole-dipole interaction between the Rb and F nuclei, in which $\mathbf{r}$ is the internuclear distance, $g_1$ and $g_2$ are the gyromagnetic ratios for the Rb and F nuclei respectively, and $\mu_N$ is one nuclear magneton.[8]

Several vibrational states and two rotational states are expected to be present in the refocused beam, so the observed spectrum will be a superposition of lines from molecules in these different rotational and vibrational states. Hence we shall observe the variation of the terms appearing in the Hamiltonian with vibrational and rotational state.

TABLE I. Quadrupole interactions of $Rb^{85}$ in $Rb^{85}F$ and of $Rb^{87}$ in $Rb^{87}F$.

| | Line | Rotational state | Transition $F_1\rightarrow F_1'$ | Vibrational state | Line frequency (center of line*) in Mc./sec. | Quadrupole interaction $-(eq_1Q_1/h)$ in Mc./sec |
|---|---|---|---|---|---|---|
| $Rb^{85}F$ | ${}^0II_1$ | 1 | $3/2\rightarrow 7/2$ | 0 | 6.328 | 70.312 |
| | ${}^1II_1$ | 1 | $0.09(eq_1Q_1/h)$ | 1 | 6.259 | 69.544 |
| | ${}^2II_1$ | 1 | | 2 | 6.184 | 68.712 |
| | ${}^3II_1$ | 1 | | 3 | 6.119 | 67.988 |
| | ${}^4II_1$ | 1 | | 4 | 6.048 | 67.200 |
| | ${}^0II_2$ | 1 | $5/2\rightarrow 7/2$<br>$0.21(eq_1Q_1/h)$ | 0 | 14.800 | 70.476 |
| | ${}^0II_3$ | 1 | $3/2\rightarrow 5/2$ | 0 | 21.103 | 70.344 |
| | ${}^1II_3$ | 1 | $0.3(eq_1Q_1/h)$ | 1 | 20.863 | 69.544 |
| | ${}^2II_3$ | 1 | | 2 | 20.632 | 68.774 |
| $Rb^{87}F$ | ${}^0I_1$ | 1 | $1/2\rightarrow 5/2$ | 0 | 6.800 | 34.000 |
| | ${}^1I_1$ | 1 | $0.2(eq_1Q_1/h)$ | 1 | 6.725 | 33.626 |
| | ${}^2I_1$ | 1 | | 2 | 6.640 | 33.200 |
| | ${}^0I_2$ | 1 | $3/2\rightarrow 5/2$ | 0 | 8.520 | 34.080 |
| | ${}^1I_2$ | 1 | $0.25(eq_1Q_1/h)$ | 1 | 8.425 | 33.700 |
| | ${}^2I_2$ | 1 | | 2 | 8.330 | 33.320 |
| | ${}^0I_3$ | 2 | $1/2\rightarrow 5/2$ | 0 | 14.570 | 33.996 |
| | ${}^1I_3$ | 2 | $3/7(eq_1Q_1/h)$ | 1 | 14.418 | 33.642 |
| | ${}^2I_3$ | 2 | | 2 | 14.250 | 33.250 |
| | ${}^0I_4$ | 1 | $1/2\rightarrow 3/2$ | 0 | 15.319 | 34.042 |
| | ${}^1I_4$ | 1 | $0.45(eq_1Q_1/h)$ | 1 | 15.143 | 33.552 |
| | ${}^2I_4$ | 1 | | 2 | 14.971 | 33.268 |

* See text for further discussion of how the "centers" of the lines are chosen.

In the application of the perturbation theory to the calculation of the eigenvalues of (1), it is important to know that $|eq_1Q_1|\gg|c_2|$ and $(g_1g_2\mu_N^2/r^3)$. Furthermore, the electric field intensity is such in our experiments that either:

$$\mu^2E^2/(\hbar^2/2A)\ll|c_2| \quad \text{("very weak" field)} \quad (a)$$

or

$$|eq_1Q_1|\gg\mu^2E^2/(\hbar^2/2A)\gg|c_2| \quad \text{("weak" field).} \quad (b)$$

In both cases there is a strong coupling of $\mathbf{I}_1$ and $\mathbf{J}$, which is the electrical quadrupole interaction associated with Rb; hence there is a well-defined $\mathbf{F}_1=\mathbf{I}_1+\mathbf{J}$ vector. We regard the zeroth order part of our Hamiltonian as:

$$\mathcal{H}_0=\frac{\hbar^2}{2A}\mathbf{J}^2-\frac{eq_1Q_1}{2I_1(2I_1-1)(2J-1)(2J+3)}\times\{3(\mathbf{I}_1\cdot\mathbf{J})^2+\tfrac{3}{2}(\mathbf{I}_1\cdot\mathbf{J})-\mathbf{I}_1^2\mathbf{J}^2\} \quad (2)$$

$\mathcal{H}_0$ has only diagonal matrix elements in a representation $(I_1, J, F_1, m_{F_1})$, in which $m_{F_1}$ is the projection of $F_1$ in the field direction. These energy values depend upon $F_1$ but are degenerate in $m_{F_1}$. In case (a) $\mathbf{F}_1$ and $\mathbf{I}_2$ are coupled by the internal interactions involving $\mathbf{I}_2$ (4th and 5th terms in (1)) to form a total angular momentum $\mathbf{F}=\mathbf{F}_1+\mathbf{I}_2$. In a representation $(I_1, J, F_1, I_2, F, M)$, in which $M$ is the projection of $\mathbf{F}$ in the field direction, the first and third terms in the Hamiltonian (1) are diagonal. The diagonal matrix elements of the fourth

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[5] J. Bardeen and C. H. Townes, Phys. Rev. **73**, 97 (1948). Note that in the initial report of this research in the abstracts of the June, 1949, American Physical Society meeting at Cambridge, $q'$ rather than $q_1$ was used. ($q'=q_1/2e$ in which $e$ is the proton charge.) Since our first report it has been agreed in this laboratory, in the interests of uniformity, to use $q$ as defined by Bardeen and Townes.

[6] H. Foley, Phys. Rev. **72**, 504 (1947).

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

[8] Kellogg, Rabi, and Ramsey, Phys. Rev. **72**, 1075 (1947).

and fifth terms of (1) depend on $F$ but not on $M$. There are off-diagonal elements of the fourth and fifth terms in (1) which connect different $F_1$ states, but these are neglected in our computations. The $-\boldsymbol{\mu}\cdot\mathbf{E}$ interaction has no diagonal matrix elements in this representation, and its effect is computed by second-order perturbation theory. The degeneracy for different $M$ values is partially removed by the field interaction, but states differing only in the sign of $M$ still remain degenerate. In case (b) we use a representation $(I_1, J, F_1, m_{F_1}, I_2, m_2)$ in which $m_2$ is the projection of $\mathbf{I}_2$ in the field direction. The first and third terms in (1) have only diagonal matrix elements and are considered first. The interaction with the field, $-\boldsymbol{\mu}\cdot\mathbf{E}$, is computed by second-order perturbation theory and finally the effects of the $c_2(\mathbf{I}_2\cdot\mathbf{J})$ interaction and of the nuclear dipole-dipole interaction are considered as smaller perturbations which couple $\mathbf{F}_1$ and $\mathbf{I}_2$. The field interaction is the same for states with $+m_{F_1}$ and $-m_{F_1}$ and the interactions involving $\mathbf{I}_2$ are the same for states with the same value of the product $m_{F_1}m_2$. Hence some degeneracy remains even after all interactions have been considered. The eigenvalues and eigenfunctions for the two cases are given in detail elsewhere.[9,10]

## IV. ANALYSIS OF SPECTRUM

### (A) Spectrum of $\mathrm{Rb}^{85}\mathrm{F}$

The lines assigned to the more abundant (73 percent) molecular species $\mathrm{Rb}^{85}\mathrm{F}$, in which the Rb nucleus has a spin of 5/2, are shown in Fig. 1. The three line groups, designated $II_1$, $II_2$, and $II_3$, are assigned to rotational state $J=1$. The uniqueness of this assignment rests on the facts that: (1) Only a few of the lower rotational states can be present in the refocused beam because only these are deflected sufficiently to get around the wire stop. Indeed only rotational states $J=1$ and $J=2$ are known to have been refocused as yet in electrical resonance experiments. (2) The spectral pattern is different for different rotational states.

The lines within a group are assigned to different vibrational states as indicated by numbers written directly above the lines. There is a fine structure for the lines which is not indicated in Fig. 1. This structure is due to the $-(\boldsymbol{\mu}\cdot\mathbf{E})$ interaction and to the fourth and fifth terms in the Hamiltonian (1), and will be discussed in the next paragraphs.

The positions of the lines are determined primarily by the change in the electrical quadrupole interaction-energy of Rb-term (3) in Hamiltonian (1). This change can be designated by the two $F_1$ values involved and in Table I the transition to which each line corresponds is indicated. The line frequency is taken at the center of the fine structure and on this basis the electrical quadrupole interaction constant is calculated. The reliability of the values shown for the interaction constants can only be evaluated after we have discussed the fine structure of the lines; however, it can be remarked that the equality of the quadrupole interaction constants evaluated from the different line groups is the proof that the identification of the observed lines with certain transitions is correct.

That the quadrupole interaction constant, $eq_1Q_1/h$, must be negative will now be shown with the aid of Fig. 2. It is to be remembered that transitions between states at low fields will be observed only if the two states involved correspond to states with different $|m_J|$ at high fields.[3] It is seen from Fig. 2, which is drawn for $eq_1Q_1/h<0$, that transitions from the levels $F_1=3/2$ to $F_1=7/2$ will be observable. If a diagram similar to Fig. 2 is drawn for the case in which $eq_1Q_1/h>0$, then it will be seen that a transition from a state with $F_1=3/2$ to a state with $F_1=7/2$ would be between two states which at high fields had $|m_J|=1$, and hence

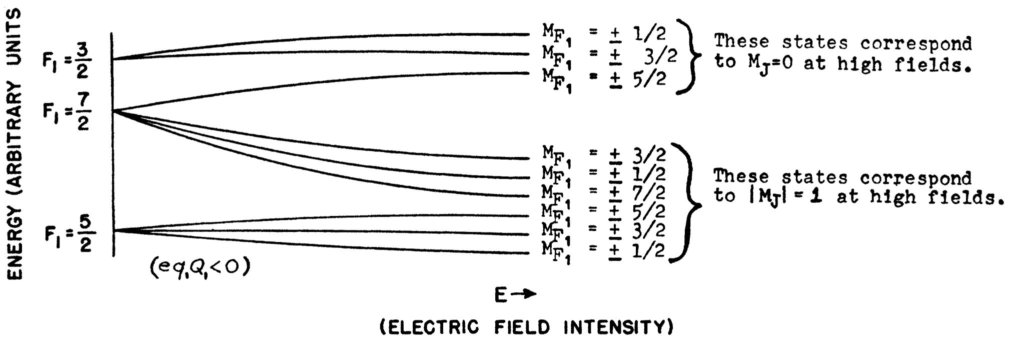

FIG. 2. A diagram indicating which low field states of $\mathrm{Rb}^{85}\mathrm{F}$ go into states with $M_J=0$ at high fields and which go into states with $|M_J|=1$. ($M_J$ is the projection of $\mathbf{J}$ in the field direction—$M_{F_1}$ is the projection of $\mathbf{F}_1$ in the field direction.) States with $J=1$ and $I_1=5/2$ are shown. An adiabatic change in the field parameter is assumed. The level spacings are not drawn to scale and there may be some crossing of levels with different $MF_1$ values, but these matters are not important to the discussion for which this figure is used. The correct ordering of the levels at high and low fields is shown. See reference 10 for the method of establishing the correspondence between low and high field states.

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[9] Nierenberg, Rabi, and Slotnick, Phys. Rev. **73**, 1430 (1948).

[10] V. Hughes and L. Grabner (to be published).

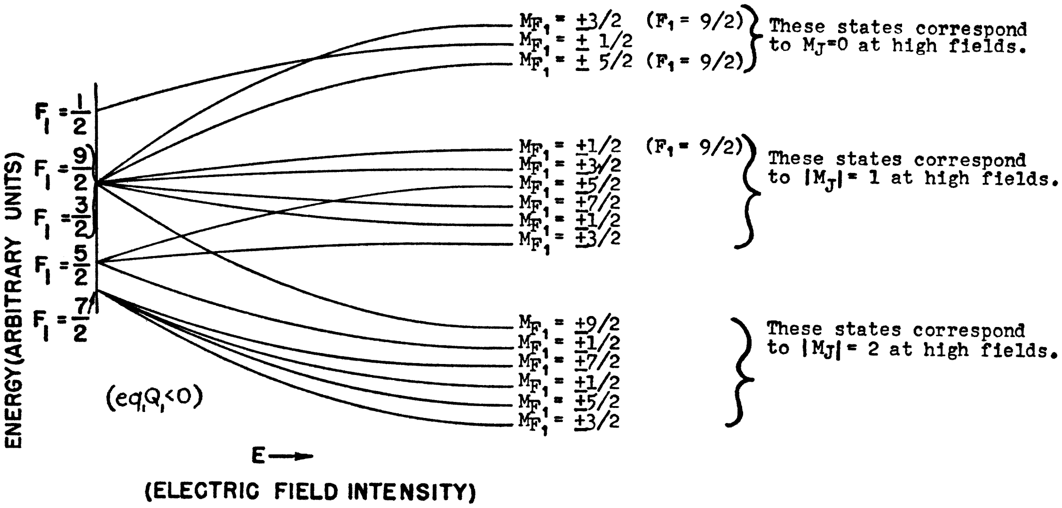

FIG. 3. A diagram indicating the correspondence between low and high field states for Rb$^{85}$F ($I_1=5/2$, $J=2$). Other remarks apply as given in Fig. 2.

would not be observed. Since this transition was observed experimentally, $eq_1Q_1/h$ must be negative.[11]

The number of line groups observed will now be considered in view of the selection rules and with the assumption of the observability criterion.[12] For the rotational state $J=1$ three transitions are allowed and all three were observed. It can be noted from Fig. 2 that the transition $F_1=5/2$ to $F_1=7/2$ is expected to be weak because most of the component lines are nonobservable; it is indeed true that this line is of weak intensity. The non-appearance of any $J=2$ lines for Rb$^{85}$F can be made plausible with the aid of Fig. 3. It is pointed out in reference 3 that because of the nature of the refocusing process if the observability criterion holds a transition at low fields will be observed only if it is between two states which at high fields correspond to $m_J=0$ and $|m_J|=2$. Of the seven lines allowed by the selection rule $\Delta F_1=\pm 1$, $\pm 2$ four will not be observed because they do not satisfy the above condition. Three transitions—($F_1=1/2$, to $F_1=5/2$), ($F_1=9/2$ to $F_1=7/2$), and $F_1=9/2$ to $F_1=5/2$)—satisfy the observability requirement but they would be expected to be weak lines for the following reasons:

(a) Only a few of the component lines for these $F_1$ transitions fulfil the observability requirement.

(b) The fraction of the total number of $J=2$ state molecules issuing from the oven that appear in the refocused beam is smaller than the analogous fraction for $J=1$ state molecules, because a larger fraction of $J=2$ state molecules impinge on the wire stop. Hence it is expected that these lines would be weak, and they were not observed at all.

## Fine Structure

For a study of the fine structure we consider the line group $II_1$ (Fig. 4) which was taken under "very weak" field conditions. Five lines were observed corresponding to vibrational states $v=0$ to $v=4$; each line is a doublet with a separation between the two components of about 20 kc/sec. The interaction of the electric field with the molecule is less than 1 kc/sec., and hence is negligible.[13]

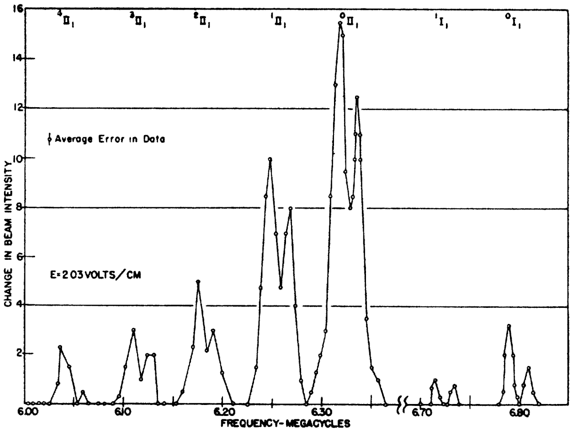

FIG. 4. Detailed spectrum of line groups $II_1$ and $I_1$ (see Table I). For line group $I_1$ radiofrequency field, $E_{rf}\sim 4$ volts/cm: for line group $II_1$, $E_{rf}\sim 8$ volts/cm. Change in beam intensity is expressed in cm of deflection on a galvanometer scale.

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[11] The correspondence between states at low fields and at high fields which must be known in order to draw a figure such as figure 2 is established by the requirements that a state has the same $m_{F_1}$ value at all fields and that states with the same $m_{F_1}$ values cannot cross. See reference 10.

[12] See reference 10. The selection rule is $\Delta F_1=0$, $\pm 1$, $\pm 2$. The transitions with $\Delta F_1=0$ would involve frequencies of the order of the fine structure of our lines; such transitions were not studied. The observability criterion is that transitions will be observed only if they occur between states which can be adiabatically transformed into states at high fields with the proper $|m_J|$ values for the refocussing process. The existence of the refocused beam $(1, \pm 1)_A-(1, 0)_B$ indicates the occurrence of nonadiabatic transitions in the interfield, regions and hence it may be that the observability criterion is not strictly applicable. For further discussion see references 3 and 10.

[13] This interaction is calculated using a value for $\mu$ of 10.6 debye.

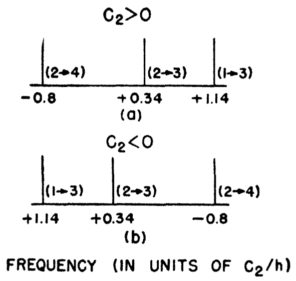

FIG. 5. Line splitting predicted from interaction $c_2(\mathbf{I}_2\cdot\mathbf{J})$ for transition $F_1=3/2$ to $F_1=7/2$ of $\mathrm{Rb}^{85}\mathrm{F}$ ($J=1$). The transition in $F$ value is indicated in parentheses. Figure (a) applies when $c_2>0$ and figure (b) applies when $c_2<0$. No attempt is made to indicate relative line intensities. Zero value for the abscissa refers to the line position due to the quadrupole interaction alone.

TABLE II. Internal interactions of $\mathrm{Rb}^{85}\mathrm{F}$ and $\mathrm{Rb}^{87}\mathrm{F}$.

| | Rotational state | Vibrational state | Quadrupole interaction $-eq_1Q_1/h$ in Mc./sec. | $\lvert c_2/h\rvert$ kc/sec. |
|---|---|---|---|---|
| | 1 | 0 | 70.31±0.10 | 11±3 |
| | 1 | 1 | 69.54±0.10 | 13±3 |
| $\mathrm{Rb}^{85}\mathrm{F}$ | 1 | 2 | 68.71±0.10 | 10±3 |
| | 1 | 3 | 67.99±0.10 | 10±3 |
| | 1 | 4 | 67.20±0.10 | 14±4 |
| | 1 | 0 | 34.00±0.06 | 14±4 |
| | 1 | 1 | 33.63±0.06 | 14±4 |
| $\mathrm{Rb}^{87}\mathrm{F}$ | 1 | 2 | 33.20±0.06 | — |
| | 2 | 0 | 34.00±0.06 | — |
| | 2 | 1 | 33.62±0.06 | — |
| | 2 | 2 | 33.25±0.06 | — |

It is natural to assume that the doublet should arise from an interaction involving the fluorine nucleus. Two such interactions are given in the fourth and fifth terms of the Hamiltonian of Eq. (1). Using the known values of $g_1$ and $g_2$[14] and a calculated value of the internuclear distance,[15] it is found that the maximum splitting that the nuclear dipole-dipole interaction can produce is about 1 kc/sec. Hence the major portion of the splitting must be assigned to the spin-orbit interaction between the $F$ nucleus and the molecular rotational angular momentum.

Since this line group was taken under "very weak" field conditions, an appropriate representation for the states involved is $(I_1, J, F_1, I_2, F, M)$; the energy depends on $M$ only because of the field interaction. The transition is $F_1=3/2$ to $F_1=7/2$ so the states involved are $(5/2, 1, 3/2, 1/2, 1, M)$, $(5/2, 1, 3/2, 1/2, 2, M)$ and $(5/2, 1, 7/2, 1/2, 3, M)$, $(5/2, 1, 7/2, 1/2, 4, M)$. The general selection rule allows $\Delta F=0, \pm1, \pm2$ but not[12] $\Delta F=\pm3$, so three components are allowed for the line of each vibrational state. Actually, the lines are split into two components with the larger intensity component appearing at the lower frequency.

The line splitting expected for the $c_2(\mathbf{I}_2\cdot\mathbf{J})$ interaction is shown in Fig. 5 for the cases of $c_2$ negative and positive. The positions of the three component lines were computed from the weak field formula given in reference 9. A half-width of about 10 kc/sec is predicted for our lines from the relationship $\Delta\nu\Delta t\sim1$ in which $\Delta\nu$ is the half width in c.p.s. and $\Delta t$ is the time spent by the molecule in the $C$-field.[2] Thus in view of the magnitude of the observed line splitting (~20 kc/sec) we would not expect to resolve the two closer-lying component lines $(F=3\rightarrow F=1)$ and $(F=3\rightarrow F=2)$. One of the lines of the observed doublet must therefore be regarded as the superposition of the two line components $(F=3\rightarrow F=1)$ and $(F=3\rightarrow F=2)$.

To say which of the two observed lines corresponds to the transition $(F=4\rightarrow F=2)$ requires a theory of relative line intensities. It does not seem, however, that experimental conditions are sufficiently well known to allow such a theory. Thus non-adiabatic transitions are known to occur in the absence of an applied radiofrequency field as the molecule traverses the apparatus, and such transitions could affect relative line intensities. It is believed that these transitions occur in the interfield region between the $A$ and $C$ fields, but little is known of their exact character. Furthermore, the amplitude of the radiofrequency field at the position of the beam is adjusted so that the transition probability is believed to be rather high. But the r-f amplitude is not sufficiently well known so that relative transition probabilities can be calculated. Several simplifying assumptions have been tried, but none of them explained the relative intensity data for the $c_2(\mathbf{I}_2\cdot\mathbf{J})$ splitting in both the $\mathrm{Rb}^{85}\mathrm{F}$ and $\mathrm{Rb}^{87}\mathrm{F}$ spectra. A further discussion of relative line intensities is given in reference 10.

The inability to say which of the two observed lines corresponds to the transition ($F=2$ to $F=4$) means that only the absolute value of $c_2/h$ can be determined. If we assume that either one of the observed lines appears midway between the predicted positions of the transitions $(F=3\rightarrow F=1)$ and $(F=3\rightarrow F=2)$—i.e. at $0.74\ c_2/h$—and that the other observed line appears at the position of the transition $(F=4\rightarrow F=2)$—i.e. at $-0.8c_2/h$—we easily compute that $\lvert c_2/h\rvert=(11\pm3)$ kc/sec. for vibrational state $v=0$. The results for the other vibrational states as well are given in Table II. The limiting error of ±3 kc/sec. is assigned because of

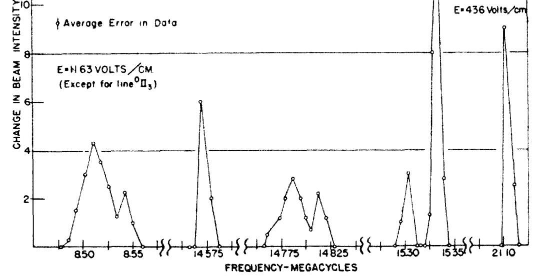

FIG. 6. Detailed spectrum of zeroth vibrational state lines for several line groups (see Table I). $E_{rf}\sim4$ volts/cm. Change in beam intensity is expressed in cm of deflection on a galvanometer scale.

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[14] J. B. M. Kellogg and S. Millman, Rev. Mod. Phys. **18**, 323 (1946).

[15] Schomaker and Stevenson, J. Am. Chem. Soc. **63**, 37 (1941).

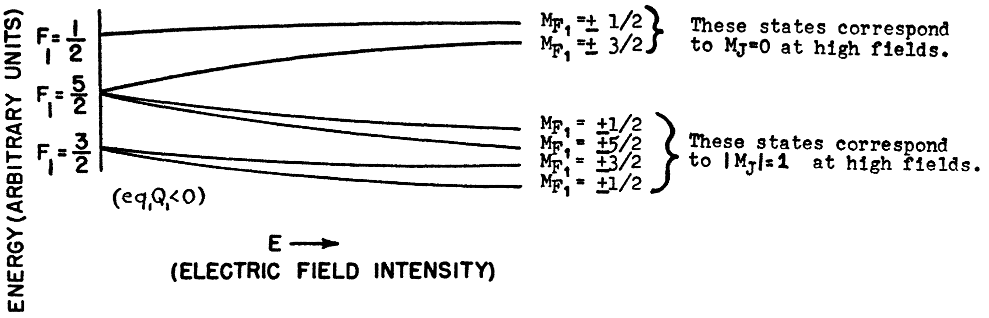


FIG. 7. A diagram indicating the correspondence between low and high field states for Rb$^{87}$F ($I_1=3/2$, $J=1$). Other remarks apply as given in Fig. 2.

the uncertainty in the peak positions of the observed lines and because of the uncertainty as to whether the observed line which corresponds to the transitions ($F=3\rightarrow F=1$) and ($F=3\rightarrow F=2$) appears exactly at the midpoint between the predicted positions of these two transitions.

We can now discuss the accuracy with which the determination of the quadrupole interaction constant is made. Our understanding of the fine structure splitting of the $F_1=7/2$ to $F_1=3/2$ line allows us to specify the position at which this line would appear in the absence of the $c_2(\mathbf{I}_2\cdot\mathbf{J})$ interaction. These frequencies are given in Table I for the line group $II_1$ and are called the positions of the "centers" of the lines. Because of the experimental uncertainty in the determination of the peaks of the lines, these positions can only be given to $\pm 5$ kc/sec. This implies that the quadrupole interaction constant can be given to about $\pm 0.1$ percent. Another source of error arises from the theory used, which neglected off-diagonal matrix elements of the quadrupole operator connecting different $J$ states.[16] The percentage error thus introduced is of the order of the quadrupole interaction energy divided by the energy difference between rotational states $J$ and $J+2$ and for our case is about 0.1 percent. The correction of the theory has not been made because the error introduced is of the order of the error in the experimental data.

Little can be learned from the fine structure of the other Rb$^{85}$F lines, because both lines were obtained under electric field conditions such that the $(\boldsymbol{\mu}\cdot\mathbf{E})$ term as well as the small internal interactions (terms (4) and (5) in Hamiltonian (1)) contribute significantly to the fine structure. The zeroth vibrational states of the two other line groups ($II_2$ and $II_3$) assigned to Rb$^{85}$F are shown in Fig. 6. Line $^0II_3$ was obtained for a field condition intermediate between "very weak" and "weak." It is a superposition of some 10 unresolved components which are produced by a splitting due to the field interaction of 10 kc/sec. and by a splitting due to the $c_2(\mathbf{I}_2\cdot\mathbf{J})$ interaction of 8 kc/sec. Line $^0II_2$ was obtained under "weak" field conditions and is composed of 4 components with a total width of about 40 kc/sec. In the observed structure there also occurs the vibrational state $v=3$ for line group $I_4$ of Rb$^{87}$F. Line $^0II_2$ appears with low intensity and the higher vibrational states were not observed. The positions of the centers of the lines in line groups $II_2$ and $II_3$ (defined as the centers of the observed structures) provide confirmation for the values of the quadrupole interaction constants determined from line group $II_1$ (See Table I).

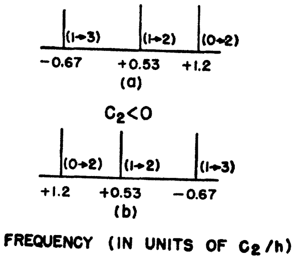
## (B) Spectrum of Rb$^{87}$F

We consider those lines in the spectrum which are assigned to the less abundant (27 percent) molecular species Rb$^{87}$F (see lines designated by $I$ in Fig. 1). The nucleus Rb$^{87}$ has a spin of 3/2; hence we expect the spectrum of Rb$^{87}$F to be similar to that of K$^{39}$F which is reported upon in detail in another paper.[3] Indeed, four line groups were observed under low electric field conditions as was also the case for K$^{39}$F. Three of these groups, designated $I_1$, $I_2$, and $I_4$, are assigned to rotational state $J=1$; and line group $I_3$ is assigned to rotational state $J=2$.

The transition in $F_1$ value to which each line corresponds is indicated in Table I. The quadrupole interaction constants are calculated by taking as the line positions the centers of the fine structure of the lines. The sign of the quadrupole interaction constant, $eq_1Q_1$, is determined to be negative by the existence of the line group $F_1=1/2$ to $F_1=5/2$, as explained in reference 3 (see Fig. 7). The argument is similar to that used earlier in this paper to prove that the quadrupole interaction constant for Rb$^{85}$F is negative.

The number of line groups expected on the basis of

FIG. 8. Line splitting predicted from interaction $c_2(\mathbf{I}_2\cdot\mathbf{J})$ for transition $F_1=1/2$ to $F_1=5/2$ of Rb$^{87}$F$(J=1)$. The transition in $F$ value is indicated in parentheses. Figure (a) applies when $c_2>0$ and figure (b) applies when $c_2<0$. No attempt is made to indicate relative line intensities. Zero value for the abscissa refers to the line position due to the quadrupole interaction alone.



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[16] See U. Fano, J. Research Nat. Bur. Stand. 40, 215 (1948).

the observability criterion were observed. For the rotational state $J=1$ three transitions are allowed and all three were observed.[12] For the rotational state $J=2$ five transitions are allowed;[12] two of these are coincident with transitions for the $J=1$ state and a third is observed.[17] The other two allowed transitions for the $J=2$ state were not observed because they occur between states which experience the same deflection in the $B$ field; i.e., have the same value of $|m_J|$ at high fields. This matter is discussed in detail in reference 3 for the exactly similar case of $K^{39}F$, and an analogous discussion has been given earlier in this paper for the isotopic species $Rb^{85}F$.

### Fine Structure

The fine structure of $Rb^{87}F$ is similar to that of $Rb^{85}F$. Line group $I_1$, shown in Fig. 4, was taken under "very weak" field conditions for which the effect of the field term is negligible. Two lines were observed corresponding to vibrational states $v=0$ and $v=1$.[18] The doublet character of the lines is due primarily to the interaction $c_2(\mathbf{I}_2\cdot\mathbf{J})$. The contribution to the splitting caused by the nuclear spin-spin interaction is less than 1 kc/sec.

The line splitting expected for the $c_2(\mathbf{I}_2\cdot\mathbf{J})$ interaction is shown in Fig. 8 for the cases of $c_2$ negative and positive. The two component lines $(F=2\rightarrow F=0)$ and $(F=2\rightarrow F=1)$ of Fig. 8 will be unresolved, so the doublet which is observed is expected.

As in the analogous case for $Rb^{85}F$ it is not possible to say which of the two observed lines corresponds to the transition $(F=3\rightarrow F=1)$ because of the lack of understanding of line intensities. Thus only the absolute value and not the sign of $c_2/h$ can be determined. By a comparison of the observed doublet with the line pattern of Fig. 8 it is found by reasoning similar to that used for $Rb^{85}F$ that $|c_2/h|=(14\pm4)$ kc/sec. for both the $v=0$ and $v=1$ vibrational states. This value is the same within experimental error as the value of $|c_2/h|$ obtained for $Rb^{85}F$. This agreement is expected since by its nature the $c_2(\mathbf{I}_2\cdot\mathbf{J})$ interaction depends only on the fluorine nucleus and the molecular electronic configuration, and so should be substantially the same for the two isotopic species.

As for the case of $Rb^{85}F$ we use this knowledge of $c_2$ to specify the positions at which the lines $F_1=5/2$ to $F_1=1/2$ would appear in the absence of the $c_2(\mathbf{I}_2\cdot\mathbf{J})$ interaction. These positions are given as the "centers" of the lines in line group $I_1$ in Table I, and from them are computed the quadrupole interaction constants given in Table II. The accuracy with which the quadrupole interaction constants can be stated is limited in exactly the same way as for $Rb^{85}F$.

The zeroth vibrational state lines of the other $Rb^{87}F$ line groups are shown in Fig. 6 and the transitions to which they correspond are indicated in Fig. 1. They were obtained under "weak" field conditions so that the $-(\boldsymbol{\mu}\cdot\mathbf{E})$ interaction contributes significantly to the fine structure. It is predicted that line ${}^0I_2$ will be split into five components by the field interaction and the $c_2(\mathbf{I}_2\cdot\mathbf{J})$ interaction, with a separation of about 60 kc/sec. between the outermost components. This is in agreement with the observed line width, but the resolution was not sufficient to distinguish all this structure. For line ${}^0I_4$ a splitting due to the field interaction into two components of about the observed separation is predicted. Each of these components will in principle be further split by the interactions with the $F$ nucleus; the magnitude of this splitting is below the resolution of the experiment. Finally, the internal structure of line ${}^0I_3$, which is assigned to rotational state $J=2$, caused by the field interaction and by the interactions with the $F$ nucleus is less than the resolution width.

The positions of the centers of lines $I_2$, $I_3$, and $I_4$ (defined as the centers of the observed structures) confirm the values of the quadrupole constants determined from line $I_1$ (see Table I).

## V. THE EXTRA LINE

An extra line group shown in Fig. 9 was observed in the neighborhood of 3 Mc/sec. This line group appears in all detail at one half the frequency of line group $II_1$ which was shown in Fig. 4. This extra line group is not predicted from the Hamiltonian (1) for either molecular species for rotational states $J=0$ to $J=3$, and no higher rotational states are deflected sufficiently by the inhomogeneous electric fields to pass by the wire stop.

The possibility that the half frequency line could arise because of harmonics in the oscillator which provides the radiofrequency field is believed to be ruled out by the following studies. The intensity of the 6 Mc/sec. line was studied as a function of the r-f amplitude applied to the $C$ field plates and it was found that the line was of zero intensity when the r-f amplitude was a factor of ten less than that used for the data of Fig. 4. Then a low pass filter, which attenuated the amplitude of signals near 6 Mc/sec. by a factor of about 30 relative to those near 3 Mc/sec., was inserted between the oscillator and the $C$ field plates, but this had no effect on the intensity of the extra line group. Furthermore, the extra line was observed to be exactly the same when taken using two different oscillators—a GR signal generator 805$C$, and a home-made oscillator. A study of the harmonic output of these two oscillators was made; using a GR 724—A Precision Wavemeter it was found that the second harmonic output from the

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[17] It is to be remarked that the reasons mentioned earlier in the analysis of the $Rb^{85}F$ spectrum for expecting the line intensities associated with $J=2$ state transitions to be weak are applicable to $Rb^{87}F$ as well. However, a $J=2$ state transition was observed for $Rb^{87}F$ whereas none was observed for $Rb^{85}F$. It is felt that the relative line intensity problem is not well enough understood so that the non-appearance of several presumably weak lines for the $J=2$ state of $Rb^{85}F$ should be regarded as surprising.

[18] The line for vibrational state $v=2$ (Fig. 1) is not shown in Fig. 4 because this very weak line was only observed when the radiofrequency field was larger than it was for the lines shown and no fine structure was resolved.

home-made oscillator was about 1 percent, and by a measurement technique involving a radio receiver it was found that the second harmonic output from the GR 805*C* oscillator was as high as 10 percent. Both the 6 Mc/sec. and the 3 Mc/sec. lines were taken with approximately the same amplitude of the radiofrequency field as is indicated in the captions to Figs. 4 and 9. Hence, the harmonic of the 3 Mc/sec. signal could not have caused the extra line, because the 6 Mc/sec. harmonic of the 3 Mc/sec. signal would have been too low to cause a 6 Mc/sec. line of appreciable intensity. Thus it seems clear that harmonics generated by the oscillator cannot account for the extra line. And there is no other place in our circuit at which harmonics of the required amplitude would be expected to be generated, since the circuit consists simply in the connection of the output from the oscillator to the two gold-plated plates of the *C*-field.

A chemical analysis[19] of the RbF was undertaken to determine whether there were appreciable amounts of other alkali halides in the sample used. By a spectrographic analysis it was found that no other alkali was present in a concentration of greater than 1 percent, and by a precipitation test the same conclusion was reached as to the presence of other halides. Such concentrations are too small to give rise to an observable line in our spectrum. Furthermore, of course, the refocussing procedure would in general eliminate the effects of any impurities.

It was suggested by Professor I. I. Rabi that this half-frequency line might arise as a double quantum transition in which two half frequency quanta supply the energy for the transition. Transitions occur normally only because there is a perturbation of the field free state and the matrix element for a transition is proportional to $EE_{rf}\sin\omega t$ in which $E$ is the intensity of the static field and $E_{rf}$ is the maximum intensity of the radiofrequency field. If we regard the radiofrequency field as causing the perturbation of the field-free state as well as the transition, then the matrix element will be proportional to $E_{rf}^2\sin^2\omega t$, and hence there will be a resonance at $\omega/2$ whereas in the normal case there was a resonance at $\omega$. A more detailed theory of this process is found in reference 10. It is clear that this process will be important when $E_{rf}$ and $E$ are of comparable magnitude; this is indeed the case for our experiment in which computation indicated that both the static field and the radio-frequency field are of several volts/cm intensity.

The extra line was found to disappear at a somewhat higher value of $E$ ($\sim$55 volts/cm which is still a weak field condition, since the field interaction amounts only to about 750 kc/sec.), whereas the upper frequency line is present and split up in the predicted manner at this same value of $E$. The theory of the double quantum process does not predict the complete disappearance of the half-frequency line at such a low static field intensity. We were not able to determine whether the extra line was present at $E=0$ as would be expected from the theory of the double quantum transition. It should be remarked that it is often impossible to study resonance effects when the *C*-field voltage is near zero.[3]

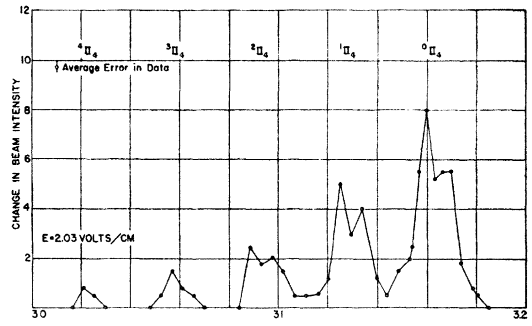

FIG. 9. Detailed spectrum of "extra" line group $II_4$. Radiofrequency field, $E_{rf}\sim 5$ volts/cm. Change in beam is expressed in cm of deflection on a galvanometer scale.

An observation which is in apparent conflict with the double quantum theory of the line origin is that the intensities of both line groups were found to vary in about the same way with the amplitude of the radiofrequency field. This observation was made with amplitudes of the radiofrequency field from $\sim$1 to 8 volts/cm for which the corresponding line intensities (in arbitrary units) varied from $\frac{1}{2}$ (which is the minimum value observable) to 12. It would be expected that the lower frequency line, for which the transition matrix element is proportional to $E_{rf}^2$, would vary more rapidly in intensity with the amplitude of the radio-frequency field than would the upper frequency line, for which the transition matrix element is proportional to $E_{rf}$. Still it should be mentioned that the transition probability is high in these experiments, so that it is not true that the transition probability is simply proportional to the square of the connecting matrix element; indeed, a near unity transition probability may obtain for the higher amplitudes of radio-frequency fields used. A much more conclusive test should be made under conditions for which the transition probability is known to be very small, but such a test will necessitate a considerable improvement in sensitivity.

Nor is it clear from the theory of the double quantum transition why only one half-frequency line group is observed rather than one for each of the seven primary line groups.

## VI. RESULTS

Table II shows the results for the internal interaction constants. The values of the quadrupole interaction constants and of $|c_2/h|$ for rotational state $J=1$ are taken from line groups $II_1$ and $I_1$ for which the field interaction is negligible. The quadrupole interaction constants for rotational state $J=2$ are obtained from

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[19] We are indebted to Professor T. I. Taylor and Mr. Robert Anderson of the Columbia Chemistry Department for performing this analysis.

line group $I_3$. The effective magnetic field produced at the $F$ nucleus by the molecular rotation can be computed from the formula:

$$H=c_2/(\mu_N g_2)$$

in which $H$ is the field per unit rotational quantum number and $\mu_N$ is 1 nuclear magneton. For $Rb^{87}F$, $H=4.5\pm1.2$ gauss and for $Rb^{85}F$, $H=3.8\pm0.9$ gauss. Within our experimental error there is no variation of $H$ with vibrational state. The errors stated for the quadrupole interaction constant and $|c_2/h|$ arise primarily from the experimental inaccuracies in the determination of line positions.

The vibrational constant, $\omega_0$, of the molecule can be determined from measured values of the relative intensities of the different vibrational lines of a line group.[2] The value obtained for $Rb^{85}F$ from a consideration of line groups $II_1$ and $II_3$ is:

$$\omega_0=(340\pm68)\text{ cm}^{-1}.$$

The electric dipole moment, $\mu$, of the molecule and the moment of inertia, $A$, can also be determined in principle by the electric resonance method, but the electrical quadrupole interactions for RbF are so large that the electric fields required for such a determination become very high. This results in a considerable decrease in line resolution, so that the accuracy of the determination would be quite poor.[3]

## VII. DISCUSSION

A primary result of these studies is the determination of the electrical quadrupole interaction constant for Rb in RbF. This constant is determined for both molecular species for rotational state $J=1$ for several vibrational states, and for $Rb^{87}F$ also for rotational state $J=2$ for several vibrational states. These interaction constants are at least an order of magnitude larger than any other quadrupole interaction constant yet reported for an alkali halide molecule, and, incidentally, for this reason have not been determined by the magnetic resonance method. The absolute value of the quadrupole interaction constant is found to decrease by about 1.1 percent from one vibrational state to the next higher one. Within the experimental accuracy no difference was observed between the quadrupole interaction constants for rotational states $J=1$ and $J=2$ for $Rb^{87}F$.

It is expected that the ratio of the quadrupole interaction constants for the two molecular species $Rb^{85}F$ and $Rb^{87}F$ is largely independent of the molecular constants, $q$. Thus the perturbation treatment of the diatomic molecule yields for the molecular wave function $\psi=\psi_{\text{electronic}}(x_i, R)\cdot\psi_{\text{vibrational}}(R)\cdot\psi_{\text{rotational}}(\theta, \phi)$ in which $x_i$ are the electron coordinates, $R$ is the internuclear distance, and $\theta$, $\phi$ are the spherical coordinate angles specifying the direction of the internuclear axis with respect to a fixed coordinate system. $\psi_{\text{electronic}}$ is independent of the reduced mass of the two nuclei. $\psi_{\text{vibrational}}$ and $\psi_{\text{rotational}}$ depend on the reduced mass of the system. The variation of $q$ from one isotopic species to the other will be caused by the variation of $\psi_{\text{vibrational}}$ and $\psi_{\text{rotational}}$. The variation of $q$ for a single molecular species has been found to be only about 1 percent from one vibrational state to another and no variation of $q$ from rotational states $J=1$ to $J=2$ was found for $Rb^{87}F$. However, the variation of $\psi_{\text{vibrational}}$ and $\psi_{\text{rotational}}$ from one vibrational or rotational state to another is much larger than the variation of these functions from one molecular species to the other. Hence it seems to be a conservative estimate that $q$ can vary by no more than 1 percent from one molecular species to the other. Thus we state $Q(Rb^{85})/Q(Rb^{87})=2.07\pm0.02$. In support of this argument there is evidence that the values of the field gradient, $q$, evaluated at the positions of the chlorine nuclei in the molecules $TlCl^{35}$ and $TlCl^{37}$ are the same.[20] For within the error of the experiment the ratio of the quadrupole interaction constants for chlorine in $TlCl^{35}$ and $TlCl^{37}$ is equal to the ratio of the electric quadrupole moments of the nuclei $Cl^{35}$ and $Cl^{37}$, which have been measured by the method of atomic beams.[21] It is interesting to note that $\mu(Rb^{85})/\mu(Rb^{87})=0.492$ where $\mu$ is the nuclear magnetic dipole moment so that $(\mu Q)Rb^{85}\simeq(\mu Q)Rb^{87}\sim1$. This is a further example of an empirical rule suggested by Gordy[22] and would indicate that the sign of the nuclear quadrupole moments of Rb is positive.

The constant $|c_2/h|$ characterizes the spin-orbit interaction between the spin of the fluorine nucleus and the rotational angular momentum of the molecule. Such an interaction in an alkali halide molecule was first reported by Nierenberg and Ramsey for LiF.[23] From their data we compute $|c_2/h|=14$ kc/sec. Trischka found $c_2/h$ to be $+16\pm2$ *kc*/sec for CsF. Our values for $|c_2/h|$ are $11\pm3$ kc/sec. for $Rb^{85}F$ and $14\pm4$ kc/sec. for $Rb^{87}F$. The magnitudes of $c_2/h$ for the RbF molecules are close to the values reported for LiF and CsF; unfortunately, the sign of $c_2/h$ was not determined in our experiment. The theory of H. M. Foley[6] attributes this $c_2(\mathbf{I}_2\cdot\mathbf{J})$ interaction to the effect of the bonding $p$ electron of the halogen atom. This theory predicts an order of magnitude for the constants $|c_2/h|$ which is in agreement with the experimental results. The magnitudes of $|c_2/h|$ for the different alkali fluorides depend upon the moment of inertia of the molecules and upon the exact molecular wave functions, and have not been computed.

We are deeply indebted to our research director, Professor I. I. Rabi, for encouragement and for many enlightening discussions. We also wish to thank Professor H. M. Foley for several helpful discussions. One of the authors (VH) is indebted to the National Research Council for the grant of a predoctoral fellowship (1946–1949).

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[20] H. Zeiger *et al.*, Bull. Am. Phys. Soc. **25**, No. 1, 35 (1950).

[21] L. Davis *et al.*, Phys. Rev. **76**, 1076 (1949).

[22] W. Gordy, Phys. Rev. **76**, 139 (1948).

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