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Molecular Beam Magnetic Resonance Spectra of $Rb^{87}F$ and $Rb^{87}Cl$ at Zero Field*

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The radiofrequency spectra of $Rb^{87}F$ and $Rb^{87}Cl$ were investigated by the zero field molecular beam magnetic resonance method. The quadrupole line was found to be split into a series of component lines. The separations between the lines, as well as the shapes of the lines, are explained by taking into account the effects of (1) a cosine coupling of the form $c_a\mathbf{I}\cdot\mathbf{J}$ between the spin of Rb^{87}, $\mathbf{I}_a$, and the rotational angular momentum of the molecule $\mathbf{J}$; and (2) the dependence of the quadrupole interaction constant eqQ on vibrational quantum number v and rotational quantum number J of the form:

$$eqQ = e\bar{q}Q + eq^{(J)}QJ(J+1) + eq^{(v)}Qv.$$

The results for Rb^{87} in $Rb^{87}F$ are: $|e\bar{q}Q|/h = 33.96 \pm 0.02$ Mc, $|eq^{(v)}Q|/h = 410 \pm 40$ kc, $|eq^{(J)}Q|/h = 26 \pm 4$ cycles/sec, $|c_a|/h = 1.1 \pm 0.1$ kc. $eq^{(v)}Q$ and $eq^{(J)}Q$ are shown to have signs opposite to that of $e\bar{q}Q$.

The results for Rb^{87} in $Rb^{87}Cl$ are: $|e\bar{q}Q|/h = 25.37 \pm 0.04$ Mc, $|eq^{(v)}Q|/h = 230 \pm 50$ kc, $|eq^{(J)}Q|/h = 12 \pm 2$ cycles/sec, $|c_a|/h = 1.0 \pm 0.1$ kc. $eq^{(v)}Q$ and $eq^{(J)}Q$ are shown to have signs opposite to that of $e\bar{q}Q$.

I. INTRODUCTION

The radiofrequency spectra of $Rb^{87}F$ and $Rb^{87}Cl$ have been observed at zero field by the molecular beam magnetic resonance method.[1–3] The observed resonance lines, corresponding to the quadrupole interaction constant of the molecule, eqQ, are found to exhibit characteristic structure which may be attributed to the effects of (1) a cosine coupling, $c_a\mathbf{I}\cdot\mathbf{J}$, between the nuclear spin of rubidium, $\mathbf{I}_a$, and the rotational angular momentum of the molecule, $\mathbf{J}$; and (2) the dependence of eqQ on the vibration and rotation of the molecule, of the form:

$$eqQ = e\bar{q}Q + eq^{(J)}QJ(J+1) + eq^{(v)}Qv.$$

The analyses of the observed lines are performed following the theory and procedure outlined in detail by Zeiger and Bolef.[4]

In the investigation of $Rb^{87}F$ by the electric resonance method,[5] an unusually large quadrupole interaction constant, $eqQ/h = 34.00$ Mc, was observed. In addition, the absolute value of the interaction constant was found to decrease about 1.1 percent (410 kc) from one vibrational state to the next higher state for the first three vibrational states. As discussed in I, the individual lines which correspond to the vibrational states of the molecule will be resolved under zero field conditions if $|eq^{(v)}Q|$ is greater than $|c_a\bar{J}|$, where $\bar{J}$ is the most probable J in the molecular beam source. For $Rb^{87}F$, $\bar{J} = 46$, while $|c_a/h|$ for the alkali halides is of the order of 1 kc. For the spectrum of $Rb^{87}F$ at zero field, therefore, a series of closely spaced "vibrational lines," each split by an $\mathbf{I}\cdot\mathbf{J}$ interaction, is predicted. Such structure was indeed observed for $Rb^{87}F$. Similar structure was observed in the spectrum of $Rb^{87}Cl$.

No spectrum for Rb^{85} in RbF and RbCl was observed. On the basis of factors contributing to the line intensity, a line intensity considerably lower than that for Rb^{87} in these molecules is predicted. These factors are discussed further in Sec. IV.

II. APPARATUS AND METHOD

The apparatus used in these investigations was the same as that described in I. The method of taking data was to vary the frequency of the oscillating field in small steps, while the homogeneous C-field was maintained at zero, and to record changes in beam intensity at the detector. The change in beam intensity at a particular value of the frequency is defined as the line intensity at that frequency. The beam intensity is expressed in centimeters deflection on a galvanometer scale.

A major difficulty in investigating the types of resonance minima observed in this experiment, broadened by the variation of eqQ with rotational and vibrational state, is the low line intensities observed. In the case of $Rb^{87}Cl$, for instance, a series of resonance minima six centimeters in depth was investigated out of a total of 2000 centimeters of refocused beam. The difference between an adjacent maximum and minimum in the pectrum was of the order of one centimeter out of a total beam of 2000 centimeters.

The conventional method of observation is that in which the detector is so placed that the reoriented molecules miss the detector. In several runs, the beam steadiness was such that the conventional method could not be used. In such instances, an alternative technique, which utilizes a detector off-set so that only a small background beam and the reoriented molecules reach the detector, was used. In this method, the detector is displaced to such a position that a maximum increase,

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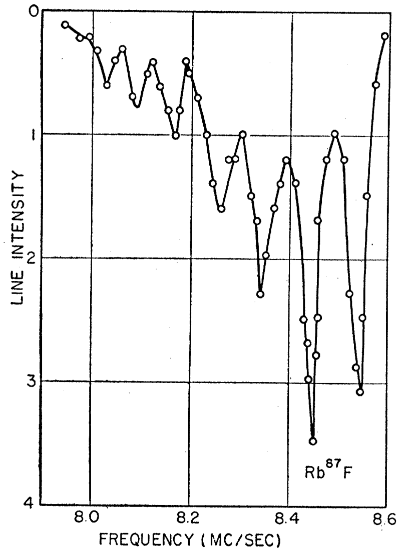

FIG. 1. Zero field spectrum of Rb^{87} in Rb^{87}F. Line intensity is expressed in centimeters deflection on a galvanometer scale. Peak intensity corresponds to a 0.2 percent change in the total beam. Radiofrequency current was 15 amperes. The widths of the lines at half-intensity are considerably greater than the 6 kc resolution half-widths expected for this molecule.

rather than a decrease, of beam intensity is observed at resonance. Thus, the resonance lines appear as peaks of beam intensity. If the deflection of the reoriented molecules at the position of the detector is not large, this method is not feasible, since in that case the detector cannot be moved far enough from the original line-up position to decrease the background appreciably. Since a large value of g_I results in a large deflection, the method works most efficiently for nuclei, such as Rb^{87} ($g_I=1.822$), with large g_I.

Measurements taken by use of both techniques during a single run indicated that the resonance curves did not differ from each other in any way but in intensity. No significant change in the position or shape of the lines was observed.

III. EXPERIMENTAL DATA

The spectrum of Rb^{87}F at zero field (see Fig. 1) differs from other zero field spectra heretofore observed[3,4] in that a large number of closely spaced lines are resolved. In the case of TlCl, discussed in I, the zero field spectrum consisted of two components, one considerably broader than the other. The shape of the spectrum was explained as that arising from a superposition of the spectra corresponding to the several vibrational states of the molecules in the beam. The resolved lines in the Rb^{87}F spectrum are relatively narrow, with half-widths of the order of 45 to 100 kc. These, however, are larger than the half-widths ($\sim$30 kc) to be expected from the values of the rf magnetic fields which induced the transitions. The separations between the component lines range from approximately 70 to 100 kc. Beginning with the most intense peak, there is an exponential decrease in intensity of the peaks toward lower frequency. The line intensity is reduced to a sufficiently low value between successive peaks to give a clear separation of the peaks.

The zero field spectrum of Rb^{87} in Rb^{87}Cl is shown in Fig. 2. The similarity between Figs. 1 and 2 is evident, and, as will be seen in Sec. V, the two spectra can be explained by similar analyses. In the case of RbCl more peaks are resolved than in the case of RbF, even though the degree of resolution is better for RbF. The rate of decrease of intensity to lower frequency from the most intense peak is less for Rb^{87}Cl than for Rb^{87}F. The widths at half-intensity are of the order of magnitude of 80 kc. Except for the separation between the first two peaks, which is 35 kc, the separation between peaks is approximately constant and of the order of 55 kc.

IV. THEORY

The energy levels of the diatomic molecules discussed here are adequately described by the Hamiltonian,

$$\mathcal{H}=\frac{-eqQ}{2I_a(2I_a-1)(2J-1)(2J+3)}\{3(\mathbf{I}_a\cdot\mathbf{J})^2+\tfrac{3}{2}(\mathbf{I}_a\cdot\mathbf{J})-I_a(I_a+1)J(J+1)\}+c_a\mathbf{I}_a\cdot\mathbf{J}+c_b\mathbf{I}_b\cdot\mathbf{J},\quad(1)$$

where the notation is that of I. In the present case, I_a is the spin of Rb, I_b that of the accompanying halogen nucleus, and J, the rotational quantum number of the molecule. The first term is the electric quadrupole interaction between the Rb nucleus and the molecular charge external to the Rb nucleus. Q is the electric quadrupole moment of the Rb nucleus, and q is the gradient, at the position of the Rb nucleus, of the

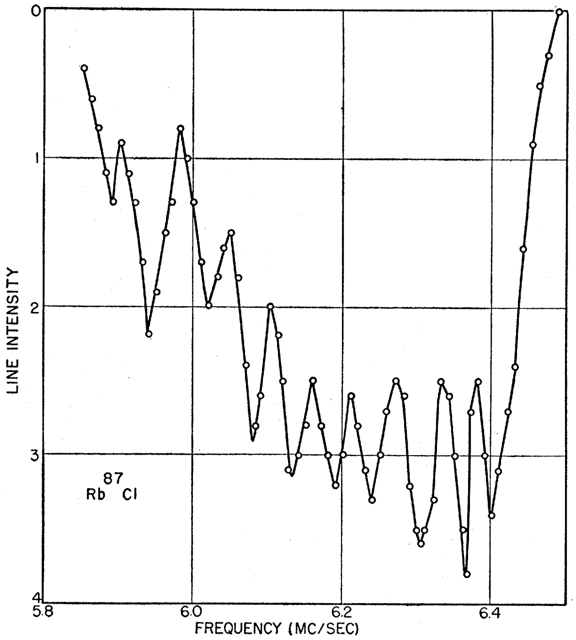

FIG. 2. Zero field spectrum of Rb^{87} in Rb^{87}Cl. Peak intensity corresponds to a 0.2 percent change in the total beam. Radiofrequency current was 15 amperes. Comparing this spectrum with that of Rb^{87}F (Fig. 1) it is seen that although more peaks are resolved, the resolution between adjacent peaks is not as good.

electric field along the internuclear axis, due to all charges external to the Rb nucleus. The second and third terms are cosine-coupling terms, the former between the spin of Rb and **J**, the latter between the spin of the halogen nucleus and **J**. The third term will be shown to have negligible effect on the observed spectra of RbF and RbCl. Similarly, in the case of RbCl, the contribution of the quadrupole moment of the Cl nucleus to the energy will be shown to be negligible. This term has been omitted from the Hamiltonian (1).

The transition energies of interest, for the case $I_a=\frac{3}{2}$, $I_b=\frac{1}{2}$, and for $J\gg 1$, are then given by,

$$W(J+\tfrac{3}{2}\leftrightarrow J+\tfrac{1}{2})=-\tfrac{1}{4}eqQ+c_a(J+\tfrac{3}{2}), \tag{2a}$$

$$W(J+\tfrac{1}{2}\leftrightarrow J-\tfrac{1}{2})=\tfrac{3}{4}eqQ(2J+1)/[(2J+3)(2J-1)]+c_a(J+\tfrac{1}{2}), \tag{2b}$$

$$W(J-\tfrac{1}{2}\leftrightarrow J-\tfrac{3}{2})=\tfrac{1}{4}eqQ+c_a(J-\tfrac{1}{2}), \tag{2c}$$

where (a) and (c) are the transitions which give rise to the lines observed in this experiment. The quadrupole portions of both (2a) and (2c) are seen to be J-independent.

For the case $I_a=5/2$, $I_b=\frac{1}{2}$, and for $J\gg 1$, the transition energies are:

$$W(J+5/2\leftrightarrow J+\tfrac{3}{2}) = (3/20)eqQ(2J+5)/(2J+3)+c_a(J+5/2), \tag{3a}$$

$$W(J+\tfrac{3}{2}\leftrightarrow J+\tfrac{1}{2}) = (3/20)eqQ(J-3)/(2J-1)+c_a(J+\tfrac{3}{2}), \tag{3b}$$

$$W(J+\tfrac{1}{2}\leftrightarrow J-\tfrac{1}{2}) = -(3/20)eqQ[4(2J+1)/(2J-1)(2J+3)]+c_a(J+\tfrac{1}{2}), \tag{3c}$$

$$W(J-\tfrac{1}{2}\leftrightarrow J-\tfrac{3}{2}) = -(3/20)eqQ(J+4)/(2J+3)+c_a(J-\tfrac{1}{2}), \tag{3d}$$

$$W(J-\tfrac{3}{2}\leftrightarrow J-\tfrac{5}{2}) = -(3/20)eqQ(2J-3)/(2J-1)+c_a(J-\tfrac{3}{2}). \tag{3e}$$

In this case the quadrupole portions of the energies are J dependent: $(dW/dJ)/dW\sim 1/J^2$ for (3a), (b), (d), (e), and $(dW/dJ)/dW\sim 1/J$ for (3c). Due to this J dependence, a broadening of the resonance minima in the spectrum of a molecule, such as $Rb^{85}F$, in which one nucleus has a spin $I=5/2$, is predicted. In general, for any value of I except $\frac{3}{2}$, the spectrum of a diatomic molecule at zero field will show a $1/J^2$ dependence. This factor, together with the effects of decreased throwout power for Rb^{85} ($g_I=0.536$ as compared with $g_I=1.822$ for Rb^{87}), and the presence of a larger number of m_I states, results in a decrease of line intensity for Rb^{85} to approximately one-sixth that observed for Rb^{87}. As a result, the spectrum of Rb^{85} in RbF and RbCl was not observed.

In the case of $Rb^{87}F$, the presence of fluorine, with spin $I=\frac{1}{2}$, will contribute an energy of the order of c_b/J to the transition energies (2a) and (2c). Since the most probable value of J is of the order of 46, and $c_b=14$ kc,[5] this term can be neglected.

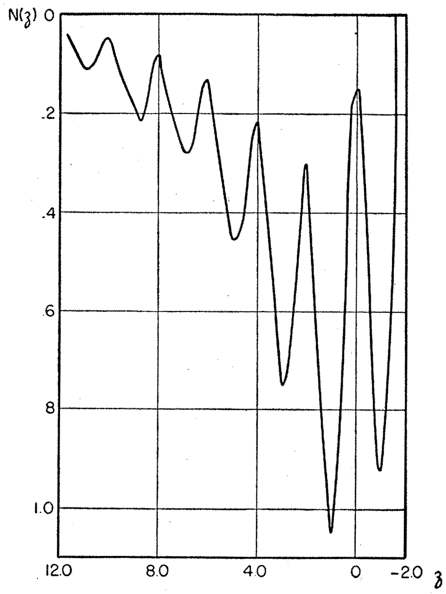

FIG. 3. Envelope of the curves corresponding to the first six vibrational states of $Rb^{87}F$, obtained by selecting $\gamma=0.30$ and following the analytical procedure described in detail in I. The first peak is the subtractive wing for the $v=0$ state. (See I, Sec. IV C, and Fig. 6.) The second peak is due to the superposition of the additive wing of the $v=0$ state and the subtractive wing of the $v=1$ state. In a similar manner, the peaks of lower intensity are obtained from a superposition of the additive and subtractive wings of higher vibrational states. This theoretical curve is to be compared with Fig. 1, the observed zero field spectrum of $Rb^{87}F$. The notation is that given in I. $N(z)=\phi\exp(-\frac{1}{2}\phi^2)/|1\mp\gamma\phi|$, where $z=\pm\phi+\frac{1}{2}\gamma\phi^2=h(f-f^0)/c_a\bar{J}$.

In the case of $Rb^{87}Cl$, c_b is not known. However, the largest known value of c_b for an alkali halide is 16 kc for CsF.[5] Assuming that c_b for $Rb^{87}Cl$ is of the same order of magnitude, and since $\bar{J}=64$ for RbCl, the term of the order of c_b/J can be neglected. As in the case of NaCl (see I), the perturbation due to a quadrupole coupling eq_bQ_b of the chlorine nucleus can be shown to contribute an energy of order $|eq_bQ_b|/J^2$ to the transition energies. From Eq. (19) of I we have the criterion, $|2eq_bQ_b/c_aJ^3|<0.05$, that this perturbation be negligible. Thus the effect of Cl on the spectrum of Rb^{87} in $Rb^{87}Cl$ is negligible if $|eq_bQ_b|\lesssim 6.5$ Mc. From the value of eqQ for Cl^{35} in KCl^{35} ($\sim$420 kc),[6] it seems probable that the above criterion is easily satisfied for $Rb^{87}Cl$.

V. ANALYSES OF $Rb^{87}F$ AND $Rb^{87}Cl$ SPECTRA

The analysis of the spectrum of $Rb^{87}F$ is made in accordance with the procedure given in I. As in the case of TlCl, the reconstruction of the experimental curve is considerably facilitated by a knowledge of the value of $eq^{(v)}Q$. From reference 5, $eq^{(v)}Q$ for $Rb^{87}F$ is taken to be 410 kc (0.012 eqQ). The ratio of intensities of the lines corresponding to successive vibrational states is given by 0.61. A value of $\gamma=0.30$ ($\gamma=2g/c\alpha$, where $\alpha=1/\bar{J}$, $g=eq^{(J)}Q/4h$, and $c=c_a/h$) was found to give

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[6] Logan, Coté, and Kusch, to be published.

TABLE I. Comparison of experimental and theoretical curves of Rb^{87}F at zero field (see Figs. 1 and 3).

Peaks		1–2	2–3	3–4	4–5	5–6
Ratio of line intensities	Exper.	0.88	1.5	1.4	1.6	1.25
	Theor.	0.88	1.4	1.6	1.7	1.3
Separation between successive peaks (kc)	Exper.	95	104	79	92	73
	Theor.	98	100	96	98	90

the best fit. This value of γ, the above values for $eq^{(v)}Q$, and the decrease of intensity per vibrational state are used to plot the curves corresponding to the states $v=0$, 1, 2, 3, 4, and 5. The envelope of these curves, as shown in Fig. 3, closely resembles the experimental curve of Rb^{87}F (see Fig. 1). The ratios of successive line intensities, as well as the separations between successive component peaks of the theoretical spectrum as compared to those of the experimental spectrum, are given in Table I. The theoretical and observed widths at half-intensity are found to be in fair agreement.

The discrepancy between the theoretical and experimental curves may be attributed to: (1) lack of precision of ω_e ($\sim 340\pm 68$ cm^{-1}) as given in reference 5, and (2) the difficulty inherent in locating the peak intensities of narrow resonance lines.

The results of the analysis are:

$$|e\bar{q}Q|/h=(33.96\pm 0.02)\text{ Mc},$$
$$|c_a|/h=1.1\pm 0.1\text{ kc},$$
$$|eq^{(J)}Q|/h=26\pm 4\text{ cycles/sec}.$$

The magnitude of the magnetic field per rotational quantum number, H_a, given by $H_a=|hc_a/g_I\mu_N|$, has the value 1.4 gauss for Rb^{87} in Rb^{87}F. Since the low frequency component of the curve corresponding to each vibrational state is broadened by the effect of the rotational variation, $eq^{(J)}Q$ has the sign opposite to that of $e\bar{q}Q$ (see I). Also, since the resonance curve tapers off gradually to low frequencies, $eq^{(v)}Q$ has the sign opposite to that of $e\bar{q}Q$. The fact that the signs of $eq^{(J)}Q$ and $eq^{(v)}Q$ are opposite to that of $e\bar{q}Q$ is in agreement with the results for all the other alkali halides investigated by the molecular beam method.[4,5]

The results for Rb^{87}Cl are obtained by a similar analysis. The results are:

$$|e\bar{q}Q|/h=25.37\pm 0.04\text{ mc},$$
$$|c_a|/h=1.0\pm 0.1\text{ kc},$$
$$|eq^{(J)}Q|/h=12\pm 2\text{ cycles/sec},$$
$$|eq^{(v)}Q|/h=230\pm 50\text{ kc}.$$

H_a for Rb^{87}Cl is 1.3 ± 0.1 gauss. The signs of $eq^{(J)}Q$ and $eq^{(v)}Q$ are both opposite to that of $e\bar{q}Q$.

The results in the case of Rb^{87}Cl are less precise than those for Rb^{87}F, primarily because of the lower line intensity and greater unsteadiness of the RbCl beam. Also, the individual peaks in the case of Rb^{87}Cl were not as well resolved as were those of Rb^{87}F.

TABLE II. Values of the coefficients $eq^{(0)}Q$, $eq^{(1)}Q$, and $eq^{(2)}Q$, in the expansion

$$eq(R)Q=eq^{(0)}Q+eq^{(1)}Q[(R-R_e)/R_e]+eq^{(2)}Q[(R-R_e)/R_e]^2+\cdots$$

for molecules investigated by the molecular beam magnetic resonance method at zero field. Since the sign of $eq^{(0)}Q$ for Rb^{87}Cl is not known, the signs of the coefficients for Rb^{87}Cl are given under the assumption that $eq^{(0)}Q$ is negative.

Molecule	$eq^{(0)}Q/h$ (MC)	$eq^{(1)}Q/h$ (Mc)	$eq^{(2)}Q/h$ (Mc)
TlCl^{35}	−15.740	−49.6	100
NaCl	−5.61[a]	24	−5.5
NaF	−8.4[a]	9.1	20
Rb^{87}Cl	(−)25.4	30.3	225
Rb^{87}F	−33.96	19.9	−21

[a] See reference 6.

VI. DISCUSSION

As is discussed in detail in I, Sec. IV B, the fact that q is a function of internuclear distance R can be expressed by the expansion

$$q(R)=q^{(0)}+q^{(1)}[(R-R_e)/R_e]+q^{(2)}[(R-R_e)/R_e]^2+\cdots, \quad (4)$$

where R_e is the equilibrium internuclear distance in the state $v=0$, $J=0$. In order for (4) to converge, the coefficients $q^{(0)}$, $q^{(1)}$, $q^{(2)}$, must all be of the same order of magnitude. Expressed in terms of measured quantities, these coefficients have the form

$$\begin{aligned} &q^{(0)}=\bar{q}-\tfrac{1}{2}q^{(v)}, \quad q^{(1)}=q^{(J)}(\omega_e/2B_e)^2, \\ &q^{(2)}=q^{(v)}(\omega_e/2B_e)-\tfrac{3}{2}q^{(1)}(1+\alpha_e\omega_e/6B_e^2), \end{aligned} \quad (5)$$

where B_e, ω_e, α_e are the usual molecular constants[7] in units of cm^{-1}. To show that the assumption that $|q^{(0)}|\sim|q^{(1)}|\sim|q^{(2)}|$ for the molecules investigated in this paper and in I is valid, these coefficients have been computed and are presented in Table II. α_e, however, is known only for TlCl. For all the other molecules given in Table II, α_e has been estimated from the Morse potential. For this reason the values of $q^{(2)}$ are much less precise than are those of $q^{(0)}$ or $q^{(1)}$.

Hughes and Grabner[5] have obtained the value of eqQ for Rb^{87} in Rb^{87}F for molecules in the zeroth vibrational state and in the first two rotational states. Since the variation of eqQ with rotational state is small, a comparison of $e\bar{q}Q$ obtained for Rb^{87} in Rb^{87}F in this experiment with the value obtained by Hughes and Grabner is valid. The value of $e\bar{q}Q=33.96\pm 0.02$ Mc in this experiment agrees well with the value of $eqQ=34.00\pm 0.06$ Mc obtained by Hughes and Grabner.

We are indebted to Professor I. I. Rabi for suggesting this problem and for his guidance throughout the course of the experiment. Professor T. Y. Wu was of great help during the early stages of the experiment. We wish to thank Professor P. Kusch and the members of the molecular beams laboratory for many helpful discussions.

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