

The quantity γ_1 is the Stark-induced decay rate involving the hyperfine levels separated by $\omega_{bc}+353-118=\omega_{bc}+235$ Mc/sec; γ_2 , the rate involving $\omega_{bc}+353+235=\omega_{bc}+588$ Mc/sec; γ_3 , the rate involving $\omega_{bc}-706-118=\omega_{bc}-824$ Mc/sec, and γ_4 , the rate involving $\omega_{bc}-706+235=\omega_{bc}-471$ Mc/sec.

Equation (18) may then be used to relate each one of the γ_i to the appropriate energy separation; $\mu_2+\mu_2^*$ is then obtainable from Eq. (26). At 7425 V/cm, the result of this procedure is that $\tau(2S)$ is decreased by only about 3 parts in 10^4 which is then neglected for the present purpose.

Hyperfine Structure of the $v=0, J=1$ State in Rb^{85}F , Rb^{87}F , K^{39}F , and K^{41}F by the Molecular-Beam Electric-Resonance Method*†

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The electric and magnetic interactions which determine the hfs of the $v=0, J=1$ state in Rb^{85}F , Rb^{87}F , K^{39}F , and K^{41}F have been obtained from spectra measured in zero magnetic field and near zero electric field. A molecular-beam electric-resonance apparatus with two-wire-type focusing fields and a single 30-cm transition field was used. For Rb^{85}F and Rb^{87}F the electric quadrupole interaction constants are $(eq_1Q_1)/h = (-70.3405 \pm 0.0004)$ Mc/sec and $(eq_1Q_1)/h = -(34.0313 \pm 0.0010)$ Mc/sec, respectively. Hence the ratio of the Rb nuclear quadrupole moments is $Q_{85}/Q_{87} = +(2.06694 \pm 0.00006)$. Comparison with data on the electric quadrupole interaction constants for Rb^{85}Cl and Rb^{87}Cl gives no evidence of a contribution from nuclear electric polarization. In Rb^{85}F , the constant of the spin-rotation interaction involving the Rb nucleus $c_1(\mathbf{I}_1 \cdot \mathbf{J})$ is $c_1/h = +(0.525 \pm 0.010)$ kc/sec, the constant of the spin-rotation interaction involving the F nucleus $c_2(\mathbf{I}_2 \cdot \mathbf{J})$ is $c_2/h = +(10.53 \pm 0.07)$ kc/sec, and the constant of the electron-coupled nuclear dipole-dipole scalar interaction $c_4(\mathbf{I}_1 \cdot \mathbf{I}_2)$ is $c_4/h = +(0.23 \pm 0.06)$ kc/sec. In Rb^{87}F , these interaction constants are $c_1/h = +(1.595 \pm 0.050)$ kc/sec, $c_2/h = +(10.51 \pm 0.08)$ kc/sec, and $c_4/h = +(0.66 \pm 0.10)$ kc/sec. The Hamiltonian also includes a nuclear dipole-dipole tensor term, and the interaction constants are $c_3/h = +(0.93 \pm 0.05)$ kc/sec and $c_3/h = +(3.16 \pm 0.18)$ kc/sec in Rb^{85}F and Rb^{87}F , respectively. These agree very well with values calculated from $(g_1g_2\mu_N^2 \langle R^{-3} \rangle_{n\nu}/h)$, so that there is no evidence for a tensor part of the electron-coupled nuclear dipole-dipole interaction in RbF. The electric quadrupole interaction constants are $(eq_1Q_1)/h = -(7932.9 \pm 0.2)$ kc/sec and $(eq_1Q_1)/h = -(9656.9 \pm 0.6)$ kc/sec for K^{39}F and K^{41}F , respectively. The ratio of the K nuclear quadrupole moments is $Q_{39}/Q_{41} = +(0.8215 \pm 0.0001)$. The observed K^{39}F spectrum also allowed the determination of the interaction constants: $c_1/h = (270 \pm 20)$ cps; $c_2/h = (10.67 \pm 0.08)$ kc/sec; $c_3/h = (540 \pm 70)$ cps; $c_4/h = (30 \pm 80)$ cps. We point out that experimental evidence for nuclear polarizability of Br nuclei is provided by data of others on the electric quadrupole interaction constants of Br^{79} and Br^{81} in the Br atom and in LiBr.

INTRODUCTION

THIS paper is divided into two parts. The first part reports a high-precision measurement of the molecular hyperfine structure of the Rb^{85}F and Rb^{87}F molecules in the vibrational state $v=0$ and the rotational state $J=1$, done by the molecular-beam electric-resonance method. This experiment is a much improved version of an older experiment by Hughes and Grabner.¹ The resolution achieved in the present experiment represents a factor of 10 improvement over the older experiment, and hence individual lines which were previously unresolved are now resolved. The second

part reports briefly on results for K^{39}F and K^{41}F . Preliminary reports of the results of the present experiment were given earlier.²

The radio-frequency spectrum observed is completely accounted for by a Hamiltonian which includes the electric quadrupole interaction with the Rb nucleus, the spin-rotation interactions with coupling constants c_1 and c_2 for Rb and F respectively, the nuclear dipole-dipole tensor interaction with coupling constant c_3 , and the scalar part of the electron-coupled nuclear dipole-dipole interaction with coupling constant c_4 . The constants c_1 , c_3 , and c_4 are determined for the first time in the RbF molecules.² The new values for the electric quadrupole interaction constants and for c_2 are more precise than the older values¹ by a factor of about 100 and the sign of c_2 is now determined.

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¹ V. W. Hughes and L. Grabner, Phys. Rev. **79**, 314 (1950).

² P. A. Bonczyk and V. W. Hughes, Bull. Am. Phys. Soc. **9**, 452 (1964); **10**, 101 (1965); P. A. Bonczyk, *ibid.* **132** (1967).

Precise values of the electric quadrupole interaction constants are of special interest in connection with observing the polarization of nuclei by molecular electric fields. A comparison of the ratio of the electric quadrupole interaction constants for Rb⁸⁵F and Rb⁸⁷F obtained in the present experiment with the corresponding ratio for Rb⁸⁵Cl and Rb⁸⁷Cl shows no evidence for the polarization of Rb nuclei in these molecules. The constants c_1 and c_2 are closely related to the magnetic shielding of the nuclei in the RbF molecules. In general, values of the molecular hfs constants are useful for testing the accuracy of molecular wave functions.

The same Hamiltonian terms are sufficient for the understanding of the K⁸⁹F and K⁴¹F spectra.

I. Rb⁸⁵F AND Rb⁸⁷F

A. Hamiltonian and Energy Levels

The part of the Hamiltonian which is relevant and sufficient for understanding the rf spectrum of RbF is given by³

$$\begin{aligned} \mathcal{H} = & -(eq_1Q_1) \frac{3(\mathbf{I}_1 \cdot \mathbf{J})^2 + \frac{3}{2}(\mathbf{I}_1 \cdot \mathbf{J}) - (\mathbf{I}_1)^2(\mathbf{J})^2}{2I_1(2I_1-1)(2J-1)(2J+3)} \\ & + c_1(\mathbf{I}_1 \cdot \mathbf{J}) + c_2(\mathbf{I}_2 \cdot \mathbf{J}) \\ & + c_3 \frac{3(\mathbf{I}_1 \cdot \mathbf{J})(\mathbf{I}_2 \cdot \mathbf{J}) + 3(\mathbf{I}_2 \cdot \mathbf{J})(\mathbf{I}_1 \cdot \mathbf{J}) - 2(\mathbf{I}_1 \cdot \mathbf{I}_2)(\mathbf{J})^2}{(2J+3)(2J-1)} \\ & + c_4(\mathbf{I}_1 \cdot \mathbf{I}_2) - \mathbf{u} \cdot \mathbf{E}. \end{aligned} \quad (1)$$

The first term is the interaction of the electric quadrupole moment Q_1 of the Rb nucleus with the electric field gradient q_1 at the nucleus due to charges in the molecule external to the nucleus. The spin of the Rb⁸⁵ nucleus is $I_1 = \frac{5}{2}$, and the spin of the Rb⁸⁷ nucleus is $I_1 = \frac{3}{2}$. The operator given is correct only for calculating matrix elements which are diagonal with respect to I_1 and J . However, since the electric quadrupole interactions are large, off-diagonal matrix elements in J must be considered and a more general Hamiltonian term is required for this purpose.⁴

A Hamiltonian term with the same dependence on the quantum numbers as given in the first term is associated with the nuclear electric polarizability energy.⁵ For this term the electric quadrupole interaction constant $-(eq_1Q_1)$ is replaced by $-\frac{2}{3}ep(\Delta\alpha)$ in which $(\Delta\alpha)$ = anisotropy of the nuclear electric polarizability and $p = 2e^{-1}\langle E_z^2 - E_x^2 \rangle_{av}$ where $\langle E_z^2 - E_x^2 \rangle_{av}$ is the average of the anisotropy of the square of the electric

field at the nucleus due to the extranuclear charges and the z axis is along the molecular symmetry axis.

The second term is the interaction of the magnetic dipole moment of the Rb nucleus with the magnetic field at the nucleus associated with the rotation of the molecule. This term is the so-called spin-rotation interaction involving the Rb nucleus. The constant c_1 may also be written as

$$c_1 = \mu_1 H_1 / I_1, \quad (2)$$

in which μ_1 is the Rb nuclear magnetic moment, and H_1 is the magnetic field at the nucleus. The third term is the spin-rotation interaction involving the F nucleus. The spin of the F nucleus is $I_2 = \frac{1}{2}$.

The fourth term is the direct or classical nuclear dipole-dipole tensor interaction. A term of this form also arises from the magnetic interactions between each nucleus and the electronic spins of its own atom together with the exchange coupling of the electronic spins with each other.⁶ The two contributions are accounted for by writing $c_3 = c_3' + c_3''$. The constant c_3' can be expressed in the familiar form

$$c_3' = g_1 g_2 \mu_N^2 \langle R^{-3} \rangle_{av}, \quad (3)$$

in which g_1 and g_2 are the g factors of the nuclei, μ_N is the nuclear magneton, and R is the equilibrium internuclear separation. The average is taken for the appropriate state of molecular vibration and rotation. The constant c_3'' is proportional to the diagonal component along the internuclear axis of the tensor for the electron-coupled nuclear dipole-dipole interaction. The fifth term is the scalar part of the electron-coupled nuclear dipole-dipole interaction.⁷

The sixth term is the interaction of the permanent electric dipole moment of the molecule with a static external electric field. For the usual value of the field in this experiment $E = 1.5$ V/cm, the Stark effect is very small.

The Hamiltonian is complete insofar as it accounts fully for the spectra. However, in principle other interactions are present which involve the coupling of higher nuclear moments with the appropriate fields at the nuclei and they have different dependences on the quantum numbers. Such interactions have not yet been observed in free molecules. But for example, the magnetic octupole interaction has been observed in free atoms.⁸

For the calculation of energy eigenvalues by perturbation theory enough is known about the relative magnitudes of the terms in the Hamiltonian to establish that the "very-weak-field" case applies and that the

³ P. Kusch and V. W. Hughes, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Heidelberg, Germany, 1959), Vol. 37/1.

⁴ J. Bardeen and C. H. Townes, *Phys. Rev.* **73**, 627 (1948); **73**, 1204 (1948).

⁵ G. R. Gunther-Mohr, S. Geschwind, and C. H. Townes, *Phys. Rev.* **81**, 289 (1951); C. H. Townes, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1958), Vol. 38/1.

⁶ N. F. Ramsey, *Phys. Rev.* **91**, 303 (1953).

⁷ Other notations have been used for c_3 and c_4 : (a) N. F. Ramsey and H. R. Lewis [*Phys. Rev.* **108**, 1246 (1957)] use $5d_1/2$ and δ ; (b) G. Gräff, W. Paul, and Ch. Schlier [*Z. Physik* **153**, 38 (1958)] use $c_3/5$ and c_4 ; (c) L. Wharton, L. P. Gold, and W. Klemperer [*Phys. Rev.* **133**, B270 (1964)] use T and J ; (4) G. Gräff and G. Werth [*Z. Physik* **183**, 223 (1965)] use d_r and d_s .

⁸ H. H. Brown and J. G. King, *Phys. Rev.* **142**, 53 (1966).

most suitable zeroth-order functions are $\Psi(J, I_1, F_1, I_2, F, M)$,⁹ where $F_1 = I_1 + J$, $F = F_1 + I_2$, and M is the magnetic quantum number associated with F .

Perturbation theory up to second-order in the electric quadrupole interaction is necessary. Matrix elements of a correct operator connecting different J states have been given.⁴ First-order perturbation theory is adequate for the second, third, fourth, and fifth terms.⁹ The diagonal matrix elements of the fifth term are

$$+\frac{1}{2}c_4 \frac{F_1(F_1+1) + I_1(I_1+1) - J(J+1)}{2F_1(F_1+1)} \times [F(F+1) - F_1(F_1+1) - I_2(I_2+1)]. \quad (4)$$

Term energies may be expressed relative to the energy of the $v=0$, $J=1$ state as linear functions of (eq_1Q_1) , c_1 , c_2 , c_3 , and c_4 to a good approximation. The results for Rb^{85}F and Rb^{87}F are given in Figs. 1 and 2, respectively. Second-order electric quadrupole interaction energies are very small, but may not be neglected. These can be numerically evaluated and shift the F_1 levels by amounts given in Figs. 1 and 2.

Transitions between hfs levels are induced by an oscillatory electric field in the C region of the apparatus. The selection rules for electric dipole transitions are: $\Delta F_1 = 0, \pm 1, \pm 2$; $\Delta F = 0, \pm 1, \pm 2$; with $\Delta M = 0, \pm 1$ for the rf field parallel and perpendicular

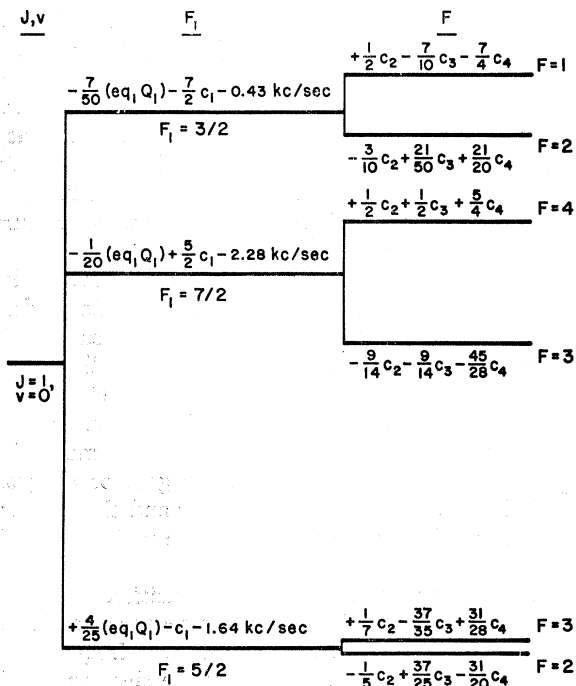


FIG. 1. Energy-level diagram for Rb^{85}F at very weak static electric field. The diagram is drawn vertically to scale, except for the splitting of adjacent F states corresponding to a given F_1 state which has been magnified by a factor of 350. F_1 level shifts due to a second-order electric quadrupole interaction are given numerically in kc/sec.

⁹ V. W. Hughes and L. Grabner, Phys. Rev. 79, 829 (1950).

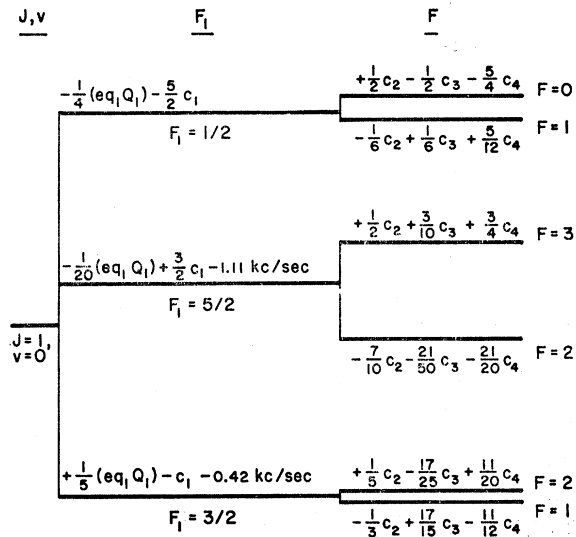


FIG. 2. Energy-level diagram for Rb^{87}F at very weak static electric field. The diagram is drawn vertically to scale, except for the splitting of adjacent F states corresponding to a given F_1 state which has been magnified by a factor of 250. F_1 level shifts due to a second-order electric quadrupole interaction are given numerically in kc/sec. (There is no such shift for the $F_1 = \frac{1}{2}$ state.)

to the static field, respectively. A small static field is present since single-quantum rf transitions are not allowed in the limit of zero field.⁹

B. Experiment

Principles

Molecules effuse from the source and pass through a foreslit into the main chamber of the apparatus shown schematically in Fig. 3. The molecular beam contains Rb^{85}F and Rb^{87}F in the ratio of their natural abundance (72% for Rb^{85}F and 28% for Rb^{87}F). The electric dipole moment μ_e effective for the deflection of a polar diatomic molecule in an inhomogeneous electric field is a function of J and its projection m_J on the electric axis of quantization. For a given (J, m_J) state, μ_e depends on the strength of the electric field in which the molecule is placed. Rb^{85}F and Rb^{87}F molecules in the same (J, m_J) state experience essentially identical deflections. A refocusing scheme with $(J, m_J)_A = (1, \pm 1)$ and $(J, m_J)_B = (1, 0)$ is used in this experiment; that is, in order to be refocused (orbit 1 in Fig. 3), the molecule must be in the state $(1, \pm 1)$ in the A field and in the state $(1, 0)$ in the B field. This is the so-called "flop-in" method of molecular-beam resonance spectroscopy. Since the directions of the gradients are the same in the A and B regions, the signs of μ_e must differ in order that the forces be oppositely directed. This is achieved by applying voltages such that μ_e is positive in the A region and negative in the B region. The stop is a razor edge

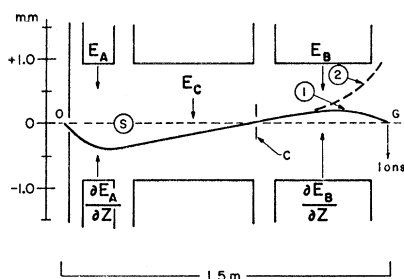


FIG. 3. Schematic diagram of the molecular-beam electric-resonance apparatus. The source is at O , and the stop is designated by S . The A and B regions have inhomogeneous electric fields. The C region has a static electric field and a superimposed 32-cm-long oscillatory electric field. The collimator is designated by c and the ion gun is at G . The ions are deflected by a magnet and then strike an electron multiplier. The trajectory of a molecule that experiences a change in quantum state in the C region is designated by 1. The trajectory of a molecule that does not experience a change in quantum state in the C region is designated by 2. The vertical scale refers only to beam trajectories and not to the field gaps.

which blocks a forward intensity of molecules in high- J states. Since μ_e is small for these molecules, they are deflected only slightly in the A field.

Radiofrequency and static electric fields are applied in the C region. Transitions are induced between hfs levels of the $v=0$, $J=1$ state. In addition to the requirement of satisfying appropriate selection rules, the observable transitions are limited to those induced from a hfs level which goes adiabatically into the state $(J, m_J) = (1, \pm 1)$ in a strong field (A field) to a level which goes adiabatically into the state $(J, m_J) = (1, 0)$ in a strong field (B field). Molecules which make an allowed transition in the C region and satisfy the above criterion for observability strike a heated tungsten filament and are ionized by the surface ionization process. Rb^+ ions are pulled out at right angles to the molecular beam by an ion gun and are focused by a mass separator onto an electron multiplier.

Molecules strike the filament even in the absence of a resonant rf field. This is due in part to the inability to discriminate perfectly against the focusing of molecules in the $J=2$ state. The mass separator makes it possible to observe the spectrum of either Rb^{85}F or Rb^{87}F without observing the background current due to the other molecule. Even with the mass separator, the background current due to the same molecule as that under study is large and unsteady. The large background is due to focused $J=2$ molecules and molecules in higher J states scattered by the stop. Vacuum fluctuations make this background unsteady. In order to cope with this problem, a synchronous narrow-band detection scheme is used.

Apparatus

The source of the molecular beam is a heated (900°K) nickel oven of conventional design.³ The oven temperature is measured with a chromel-alumel thermocouple and a mV potentiometer.

The inhomogeneous electric A and B fields are of the two-wire type.³ The length of the A field effective for the deflection of a molecule is 13 cm, and the corresponding B dimension is 41 cm. The electrodes are alloyed aluminum, and the ends nearest the C field are designed so as to minimize abrupt changes in electric field strength in the interfield regions.

The electric C field is quite similar to one described earlier.³ The principal difference is a lengthened 30-cm oscillating-field region. The electrodes are aluminum and are spaced 1 cm apart. The collimator is a 0.1-mm quartz slit.

A spurious magnetic field in the C region of even 1 G, which can originate from the earth, the mass separator and the electron multiplier, seriously perturbs the spectrum. Three orthogonal sets of Helmholtz-like coils enclose the C region (external to the vacuum) and permit reduction of the magnetic field in the C region to less than 100 mG.

The ion gun is almost identical in design to one used earlier.¹⁰ The surface-ionization detector filament is a $0.05\text{-mm} \times 0.25\text{-mm}$ tungsten ribbon which is heated to 1450°K . The resolution of mass 85 and mass 87 ions is complete in the focal plane of the mass separator. If the separator is adjusted to select mass 85, 1/15 of the mass 85 ions formed at the filament of the ion gun pass through the 1-mm slit in the focal plane and strike the input of the multiplier. If mass 87 ions are selected, the transmission efficiency is essentially the same. The ion-gun assembly is enclosed by a thin copper box, which has appropriate openings for the entrance of molecules and the emergence of ions, and it is thermally connected to a liquid-nitrogen trap. The constancy of the long-term ionization efficiency is more certain with this provision for cooling the region of ionization. Oil diffusion pumps maintain a main chamber pressure of 2×10^{-7} mm Hg.

The Bendix 306 electron multiplier depends for its operation on combined electric and magnetic fields.¹¹ The gain is independent of the length of exposure to air and is variable with voltage. We have generally used a gain of 10^6 (output electrons per secondary electron at the input). About 7 Rb^+ ions of 10^3 eV energy are necessary to produce one electron at the multiplier input. This was estimated from the gain or electron multiplication factor of the multiplier and the ion current measured near the cathode of the multiplier with an electrometer.

The rf voltage for inducing the transition is derived from a General Radio 805-C signal generator, and is on-off modulated with a mercury switch at a frequency of 19 cps. The signal at the output of the electron multiplier is amplified by a preamplifier and synchronously detected by a lock-in amplifier tuned to the modulation frequency.

¹⁰ R. Braunstein and J. W. Trischka, *Phys. Rev.* **98**, 1092 (1955).

¹¹ L. Heroux and H. E. Hinteregger, *Rev. Sci. Instr.* **31**, 280 (1960); G. W. Goodrich and W. C. Wiley, *ibid.* **32**, 846 (1961).

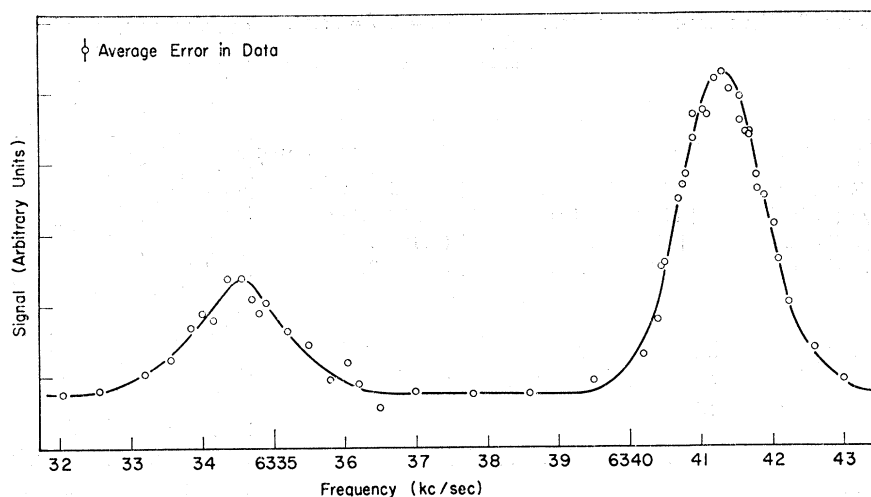


FIG. 4. Lines in the spectrum of Rb^{85}F for the transitions $(F_1, F) = (\frac{7}{2}, 3) \rightarrow (\frac{5}{2}, 2)$ and $(F_1, F) = (\frac{7}{2}, 3) \rightarrow (\frac{5}{2}, 1)$.

In some cases, it was necessary to average the output of the lock-in amplifier for about 4 min at each point on a spectral line with an amplifier time constant of 10 sec in order to have a signal-to-noise ratio greater than 15. The averaging is done with an integrating digital-voltmeter or a recorder. Frequency measurements are made with a Hewlett-Packard 5245L frequency counter. The counter accuracy is periodically checked against a National NC1001A cesium-beam frequency standard.

A more detailed description of the apparatus has been given elsewhere.¹²

Data

The principal experimental difficulty is the small signal-to-background ratio. A typical signal is a current of 2×10^{-15} A at the surface ionization detector and the background is about 2×10^{-13} A. The background is not affected by turning off the static C field but decreases to 10^{-13} A when the A field is turned off. If the stop is

positioned so as not to obstruct any part of the beam, the intensity increases to 1.5×10^{-9} A. Since considerable time is consumed in gathering the points, it is important to examine the long term stability of the signal at a fixed frequency. By continuously observing the signal at the line center for a period of 1.5 h, it was found that any change of the signal over this period of time did not exceed 2% of the signal amplitude. It was necessary to wait some 8 h after the oven was heated in order to achieve this stability.

Typical spectral lines are shown in Fig. 4. These were obtained by tuning the rf signal generator in approximately equal frequency intervals. Symmetric curves have been fit to the experimental points. The linewidth is 1.4 kc/sec which is the natural linewidth associated with the transit time. The accuracy of determining the line center is limited by the signal-to-noise ratio and is about ± 100 cps (1 standard deviation).

Each observed line is a superposition of unresolved Stark components. The static and rf electric fields in the C region were about 1.5 V/cm, and hence the Stark shifts of the component lines were generally less than 100 cps and hence could be neglected. The Zeeman effect due to the small residual magnetic field was observed to be less than about 100 cps. The Stark and Zeeman effects introduce uncertainties in the line centers of somewhat less than 100 cps.

The observed Rb^{85}F and Rb^{87}F transition frequencies are given in Table I. The identification of a transition is based largely on the work of Hughes and Grabner.¹ They resolved and measured the transitions between different F_1 levels; however, they did not resolve all the structure associated with the F levels. In the present experiment, the hfs of the F levels is resolved except for the transitions (f'_4, f'_5) and (f'_6, f'_7) . To determine the centers of the unresolved lines each component was assumed to have the natural linewidth, and the line centers and relative intensities of the components were found from a best fit to the experimental points.

TABLE I. Observed Rb^{85}F and Rb^{87}F spectra.

Molecule	Line	Transition (F_1, F) - (F_1', F')	Line center frequency (kc/sec)
Rb^{85}F	f_1	$(\frac{7}{2}, 4) - (\frac{5}{2}, 2)$	6320.80 ± 0.10
	f_2	$(\frac{7}{2}, 3) - (\frac{5}{2}, 2)$	6334.55 ± 0.15
	f_3	$(\frac{7}{2}, 3) - (\frac{5}{2}, 1)$	6341.30 ± 0.10
	f_4	$(\frac{5}{2}, 3) - (\frac{3}{2}, 3)$	$14\ 764.30 \pm 0.20$
	f_5	$(\frac{5}{2}, 2) - (\frac{3}{2}, 3)$	$14\ 766.05 \pm 0.10$
	f_6	$(\frac{5}{2}, 3) - (\frac{3}{2}, 4)$	$14\ 777.95 \pm 0.15$
Rb^{87}F	f'_1	$(\frac{5}{2}, 3) - (\frac{3}{2}, 1)$	6793.33 ± 0.10
	f'_2	$(\frac{5}{2}, 2) - (\frac{3}{2}, 1)$	6809.41 ± 0.10
	f'_3	$(\frac{5}{2}, 2) - (\frac{3}{2}, 0)$	6813.20 ± 0.10
	f'_4	$(\frac{3}{2}, 2) - (\frac{1}{2}, 2)$	8501.40 ± 0.30
	f'_5	$(\frac{3}{2}, 1) - (\frac{1}{2}, 2)$	8502.40 ± 0.30
	f'_6	$(\frac{3}{2}, 2) - (\frac{1}{2}, 3)$	8517.50 ± 0.30
	f'_7	$(\frac{3}{2}, 1) - (\frac{1}{2}, 3)$	8518.20 ± 0.30

¹² P. A. Bonczyk, Ph.D. thesis, Yale University, 1965 (unpublished).

TABLE II. Hyperfine-structure constants of the $v=0$, $J=1$ state in Rb^{85}F and Rb^{87}F .

	Rb^{85}F	Rb^{87}F
$(eq_1Q_1)/h$ (Mc/sec)	$-(70.3405 \pm 0.0004)$	$-(34.0313 \pm 0.0010)$
c_1/h (kc/sec)	$+(0.525 \pm 0.010)$	$+(1.595 \pm 0.050)$
c_2/h (kc/sec)	$+(10.53 \pm 0.07)$	$+(10.51 \pm 0.08)$
c_3/h (kc/sec)	$+(0.93 \pm 0.05)$	$+(3.16 \pm 0.18)$
c_4/h (kc/sec)	$+(0.23 \pm 0.06)$	$+(0.66 \pm 0.10)$

Enough transitions were observed for Rb^{85}F and Rb^{87}F to provide an overdetermined system for evaluating the coupling constants.

C. Results and Discussion

With the use of the observed transition frequencies as given in Table I together with the term energies as given in Figs. 1 and 2 we can determine the values of the hfs coupling constants. They are given in Table II where the indicated errors were obtained by combining quadratically the uncertainties in the line centers. For Rb^{85}F one more line was observed than was required for determination of the coupling constants and for Rb^{87}F two more lines were observed. The frequencies for these three lines predicted from the coupling constants agreed with the measured frequencies within the experimental errors. The results given in Table II are in agreement with the earlier but less precise work of Hughes and Grabner¹ and of Lew *et al.*¹³

From the data given in Table II we can compute the ratio of the electric quadrupole interaction constants: $(eq_1Q_1)_{85}/(eq_1Q_1)_{87} = +(2.06694 \pm 0.00006)$. Further discussion of this ratio will be given later in this paper.

The interaction constants c_1 and c_2 can be used in Eq. (2) to determine the magnetic fields at the nuclei. At the F nucleus in Rb^{85}F the field is $H_2 = 2.63 \pm 0.02$ G and in Rb^{87}F , $H_2 = 2.62 \pm 0.02$ G. Since the measurements were not sensitive enough to detect a very slight difference in H_2 due to unequal zero-point vibration between Rb^{85}F and Rb^{87}F , the good agreement is expected. At Rb^{85} in Rb^{85}F , $H_1 = 1.27 \pm 0.03$ G and at Rb^{87} in Rb^{87}F , $H_1 = 1.14 \pm 0.04$ G. These values of H_1 differ by $2\frac{1}{2}$ standard deviations, which is only marginally a discrepancy. If the discrepancy were real, one would suspect some inadequacy in the Hamiltonian, especially in the electric or magnetic interactions which couple I_1 to J , but no significant omission has been discovered.

The interaction constants c_3 for Rb^{85}F and Rb^{87}F are very well accounted for by the classical nuclear magnetic dipole-dipole interaction. Hence the values of the electron-coupled nuclear dipole-dipole constants c_3'' are zero within the accuracy of the experiment. The coupling constants c_4 for the scalar part of the electron-

coupled nuclear dipole-dipole interaction are relatively large for alkali halide molecules.

The values we have obtained for eq_1Q_1 and c_1 in Rb^{87}F are not in agreement with corresponding but much less precise molecular-beam magnetic-resonance measurements, which yield the magnitudes but not the signs of these interactions.¹⁴ Discrepancies of this type between electric- and magnetic-resonance work are not new, and are probably due to the complicated spectra involving many J states for the magnetic resonance experiments.

Since the submission of this paper for publication, results of other recent RbF measurements done by the molecular-beam electric-resonance method have come to our attention.¹⁵ The published results referred to in Ref. 15 include the hfs coupling constants for the $v=0$, $J=1$ state in Rb^{85}F . The values given therein are in good agreement with those obtained by us. For example, Zorn *et al.* obtain $(eq_1Q_1)/h = -(70.342 \pm 0.001)$ Mc/sec and Gräff *et al.* obtain $(eq_1Q_1)/h = -(70.3410 \pm 0.0026)$ Mc/sec.

Future Improvements in Experiment

The principal limitation in the present experiment is the small value of signal to background. The use of inhomogeneous electric four-pole A and B fields should improve the signal to background.¹⁶ A critical comparison of the signal-to-background characteristics associated with two-pole and four-pole electric deflecting fields requires the recognition that only the "flop-out" mode of operation is possible with the four-pole fields. Thus in the absence of a transition, if the molecule is in the state $(J, m_J) = (1, 0)$ in the A and B fields it will be refocused onto the detector, but if a transition occurs in the C field to a state which corresponds in high field to $(J, m_J) = (1, \pm 1)$ the molecule does not strike the detector. To provide an experimental comparison of two-pole and four-pole fields the transition at 6320.8 kc/sec in the spectrum of Rb^{85}F was observed with our apparatus set up in a "flop-out" mode of operation, and the signal and background were about the same as in the "flop-in" measurement of this transition. For our apparatus the ratio of focused $(1, 0)$ molecules to molecules in all other (J, m_J) states which strike the detector is estimated to be 0.7. By comparison, for TIF spectra measured with a four-pole focusing apparatus, this ratio is 5. Molecular constants cannot account for this difference since RbF and TlF are very similar in this respect. Hence there is a factor of 7 improvement with the use of four-pole fields. This is a useful comment on the relative merits of an apparatus with two-pole or four-pole focusing fields. A related

¹⁴ D. I. Bolef and H. J. Zeiger, *Phys. Rev.* **85**, 799 (1952).

¹⁵ J. C. Zorn, T. C. English, J. T. Dickinson, and D. A. Stephenson, *J. Chem. Phys.* **45**, 3731 (1966); G. Gräff, R. Schönwasser, and M. Tonutti, *Z. Physik* **199**, 157 (1967); A. J. Hebert (private communication).

¹⁶ R. v. Boeckh, G. Gräff, and R. Ley, *Z. Physik* **179**, 285 (1964).

¹³ H. Lew, D. Morris, F. E. Geiger, Jr., and J. T. Eisinger, *Can. J. Phys.* **36**, 171 (1958).

important point is the fact that a typical line in the TIF spectrum was measured in 1.5 min whereas an hour or more was the typical observation time in our experiment to achieve a comparable sensitivity.

Although an improvement in signal to noise with the use of four-pole fields would be valuable for rapid data acquisition, an increase in the precision of determination of line frequencies in our very weak electric field experiment would be very difficult since it would require a complete understanding of the effect of static and rf electric fields on the line shape. As mentioned, an observed line is a superposition of many unresolved Stark components. The relative intensities and centers of all the component lines would need to be known, which would require an exact knowledge of the static and rf electric fields and of the distribution of molecules in the hfs states, including the effect of Majorana transitions.

Ratio of Nuclear Electric Quadrupole Moments and Nuclear Electric Polarizability

One of the principal results of this paper is the high-precision determination of the ratio of the electric quadrupole interaction constants in Rb^{85}F and Rb^{87}F . It has been pointed out that the interaction constant (eq_1Q_1) may include a contribution due to the energy of nuclear electric polarizability. A contribution can also come from the so-called pseudoquadrupole interaction.¹⁷ We estimate that the contribution of this latter interaction to the line frequencies is less than 100 cps and hence less than the experimental error. If we ignore the contribution of nuclear polarization for the present then we can consider further the meaning of the ratio $(eq_1Q_1)_{85}/(eq_1Q_1)_{87}$. Since the electric field gradient q_1 depends only on the molecular wavefunction and not on the nuclear moments, we can expect that the values of q_1 for Rb^{85}F and Rb^{87}F are nearly equal and hence the ratio of the electric quadrupole interaction constants will be the ratio of the nuclear electric quadrupole moments.

However, the ratios will differ slightly because of the vibrational differences of the two molecules. An estimate of the difference can be given in the following way. We assume that q_1 is proportional to $1/R^3$.¹⁸ Then if the motion of the nuclei is governed by a Morse potential, it can be shown that the effect of zero-point vibration on R^{-3} is given by $\langle R^{-3} \rangle_{\text{av}} \approx R^{-3} [1 - 5(B/\omega)]$.¹⁹ The quantities B and ω are the known equilibrium values for the constants of rotation and vibration, and R is the equilibrium nuclear separation. The difference in $\langle R^{-3} \rangle_{\text{av}}$ between Rb^{85}F and Rb^{87}F as a result of unequal reduced masses is readily calculated to be 1 part in 10^5 . Thus, within the quoted uncertainty, the ratio of

¹⁷ H. M. Foley, Phys. Rev. **72**, 504 (1947).

¹⁸ H. M. Foley, R. M. Sternheimer, and D. Tycko, Phys. Rev. **93**, 734 (1954); R. M. Sternheimer and H. M. Foley, *ibid.* **102**, 731 (1956).

¹⁹ N. F. Ramsey, *Molecular Beams* (Oxford University Press, Oxford, England, 1956).

TABLE III. Observed K^{39}F and K^{41}F spectra.

Molecule	Transition (F_1, F)-(F_1', F')	Line center frequency (kc/sec)
K^{39}F	$(\frac{5}{2}, 3) - (\frac{3}{2}, 1)$	1578.31±0.10
	$(\frac{5}{2}, 2) - (\frac{3}{2}, 1)$	1591.56±0.10
	$(\frac{5}{2}, 2) - (\frac{3}{2}, 0)$	1598.26±0.10
	$(\frac{3}{2}, 2) - (\frac{1}{2}, 1)$	3565.93±0.10
	$(\frac{3}{2}, 1) - (\frac{1}{2}, 0)$	3577.38±0.10
K^{41}F	$(\frac{5}{2}, 3) - (\frac{3}{2}, 1)$	1923.75±0.10

the electric quadrupole interaction constants is the same as the ratio of the nuclear quadrupole moments $Q_{85}/Q_{87} = +(2.06694 \pm 0.00006)$.

The effect of nuclear electric polarization can be looked for by comparing the ratios of the electric quadrupole interaction constants for different isotopic molecules. If nuclear electric polarization is present, then the ratio of the electric quadrupole interaction constants should be modified to read⁵

$$[(eq_1Q_1)_{85} + \frac{2}{3}ep(\Delta\alpha)_{85}] / [(eq_1Q_1)_{87} + \frac{2}{3}ep(\Delta\alpha)_{87}]. \quad (5)$$

Data for a single molecular species such as RbF are not sufficient to establish the presence of nuclear electric polarization. However, if data are available on the Rb^{85} and Rb^{87} isotopes in other molecular (or atomic) species as well, then the presence of nuclear electric polarization can be exhibited as a difference in the values of the experimental ratio given above for the different species. Data are available on Rb^{85}Cl and Rb^{87}Cl and the ratio of effective electric quadrupole interaction constants for these molecules has been determined to be $(eq_1Q_1)_{85}/(eq_1Q_1)_{87} = +(2.0669 \pm 0.0005)$.²⁰ This latter value agrees with the corresponding value for RbF to within the experimental accuracy of 2 parts in 10^4 . Hence no nuclear electric polarization is exhibited.

Order-of-magnitude estimates will now be given in order to understand the absence of nuclear electric polarization. The sensitivity of this approach to detecting nuclear polarization is larger if the ratios p/q_1 are very different for the two molecular species. The difference of q_1 values for the two molecular species is given by comparing the electric quadrupole interaction constants and amounts to about 25%. A molecular model¹⁸ for calculating q_1 and p which assigns the principal contribution to a p electron gives $e^{-1}p = 10^{84} \text{ cm}^{-4}$ for RbF and p/q_1 values for the two molecular species which differ by 8%. Calculation of the nuclear electric polarizability $(\Delta\alpha)$ requires knowledge of the energies of excited nuclear states and of the electric dipole matrix elements. If the difference between $|\langle 0 | ez' | n \rangle|^2$ and $|\langle 0 | ex' | n \rangle|^2$ summed over n , which determines the anisotropy of α , is evaluated from a sum rule and an estimate²¹ for the distortion parameter

²⁰ J. W. Trischka and R. Braunstein, Phys. Rev. **96**, 968 (1954).

²¹ S. De Benedetti, *Nuclear Interactions* (John Wiley & Sons, Inc., New York, 1964), p. 113.

TABLE IV. Hyperfine-structure constants of the $v=0, J=1$ state in $K^{39}F$ and $K^{41}F$.

	$K^{39}F$	$K^{41}F$
$(eq_1Q_1)/h$ (kc/sec)	$-(7932.9 \pm 0.2)$	$-(9656.9 \pm 0.6)$
c_1/h (cps)	$+(270 \pm 20)$	$+(145 \pm 15)$
c_2/h (kc/sec)	$+(10.67 \pm 0.08)$	$+(10.50 \pm 0.08)$
c_3/h (cps)	$+(540 \pm 70)$	$+(300 \pm 40)$
c_4/h (cps)	$+(30 \pm 80)$	$+(17 \pm 50)$

β , and the principal strength of the matrix elements is taken in the region of the giant resonance at ~ 15 MeV, then we get $(\Delta\alpha)_{85} \sim (\Delta\alpha)_{87} = 10^{-38}$ cm³. Use of these estimates above indicates that the nuclear electric polarization energies will contribute about 1 part in 10^4 to the ratio given; any difference between RbF and RbCl is about 1 in 10^6 . It should be emphasized that the estimate we have given is very rough; hence the absence of an observed difference between the ratios for RbF and RbCl is consistent with the estimate given within the experimental accuracy.

There is experimental evidence for a difference in the ratio for the effective electric quadrupole interactions of Br^{79} and Br^{81} nuclei in atomic bromine and in Li^6Br with the molecular ratio being (37 ± 8) parts in 10^5 higher than the atomic ratio.^{8,22} There is a large difference between the atom and molecule with respect to the electric field gradient at the Br nucleus. As discussed, this enhances the possibility of observing nuclear polarizability, and hence we suggest that this ratio difference is due principally to this effect. Based on estimates of ρ for Br and LiBr we deduce: $(\Delta\alpha)_{79} - ((\Delta\alpha)_{81}Q_{79}/Q_{81}) = -(3 \times 10^{-38})$ cm³. If we assume that the nuclear polarizabilities of Br^{79} and Br^{81} are equal, then $(\Delta\alpha)_{79} = (\Delta\alpha)_{81} = 15 \times 10^{38}$ cm³, which is the order of the nuclear volume. Following a procedure very similar to that given for RbF, we estimate $(\Delta\alpha)_{79} = (\Delta\alpha)_{81} = 4 \times 10^{-38}$ cm³. Since these estimates are rough, the agreement is reasonable. A more precise determination of the relevant electric quadrupole interaction constants in LiBr would be very useful.

II. $K^{39}F$ AND $K^{41}F$

The measurements described in the text were extended to include the determination of the hfs of the $v=0, J=1$ state in $K^{39}F$ and $K^{41}F$ (both $I_1 = \frac{3}{2}$). Spectra were measured in near zero electric field and zero magnetic field following a procedure almost identical to that given for RbF. All of the observed rf transitions between hfs levels exhibit the natural linewidth of 2 kc/sec.

²² A. J. Hebert, F. W. Breivogel, Jr., and K. Street, Jr., *J. Chem. Phys.* **41**, 2368 (1964). Recently, an error was found in the analysis of the data of this experiment, and the subsequent corrections have the effect of lowering the difference between ratios cited above to (22 ± 8) parts in 10^5 [A. J. Hebert (private communication)].

Five lines were measured in the $K^{39}F$ spectrum and the line center frequencies are listed in Table III. The energy-level diagram is the same as that given in Fig. 2 after deletion of second-order perturbation theory contributions due to the electric quadrupole interaction. This contribution is not significant in KF since the electric quadrupole interaction is small. Enough lines of the $K^{39}F$ spectrum were measured to determine all the $K^{39}F$ hfs constants associated with the Hamiltonian. These constants are given in Table IV.

It was possible to measure only one $K^{41}F$ (7% isotopic abundance) line with good sensitivity. Hence the four $K^{41}F$ magnetic interaction constants shown in Table IV were inferred from corresponding $K^{39}F$ constants and the known values of the nuclear magnetic moments and the atomic masses.¹⁹ Using these constants and the center frequency of the measured line, the electric quadrupole interaction constant in $K^{41}F$ was determined. The ratio of the electric quadrupole interaction constants, to within the accuracy of the determination of this ratio, is the same as the ratio of nuclear quadrupole moments and hence $Q_{39}/Q_{41} = (0.8215 \pm 0.0001)$.

This measurement represents the first time that the near zero field $K^{39}F$ hfs spectrum has been fully resolved. Previous determinations of (eq_1Q_1) for the $v=0, J=1$ state in $K^{39}F$ have been made by Grabner and Hughes,²³ Schlier,²⁴ and Green and Lew²⁵ and the values obtained from these measurements are $-(7938 \pm 40)$, $-(7934.7 \pm 1.1)$, and $-(7932 \pm 3)$ kc/sec, respectively. The electric quadrupole interaction in $K^{41}F$ has been measured here for the first time. The value obtained for the ratio Q_{39}/Q_{41} agrees with the value (0.820 ± 0.002) obtained from a measurement of KCl spectra done by the molecular-beam electric-resonance method,²⁶ and, moreover, improves the precision with which this ratio is known by more than an order of magnitude. There is no evidence for electric polarization of the K nuclei in KF.

Note added in proof. Since the submission of this paper for publication, results of other recent KF measurements done by the molecular-beam electric-resonance method have come to our attention. [See Ref. 27.] The results include the hfs coupling constants for the $v=0, J=1$ state in $K^{39}F$ and the values given therein are in agreement with those obtained by us.

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²³ L. Grabner and V. W. Hughes, *Phys. Rev.* **79**, 819 (1950).

²⁴ C. Schlier, *Z. Physik* **147**, 600 (1957).

²⁵ G. W. Green and H. Lew, *Can. J. Phys.* **38**, 482 (1960).

²⁶ C. A. Lee, B. P. Fabricand, R. O. Carlson, and I. I. Rabi, *Phys. Rev.* **91**, 1395 (1953).

²⁷ R. van Wachem and A. Dymanus, *J. Chem. Phys.* **46**, 3749 (1967).