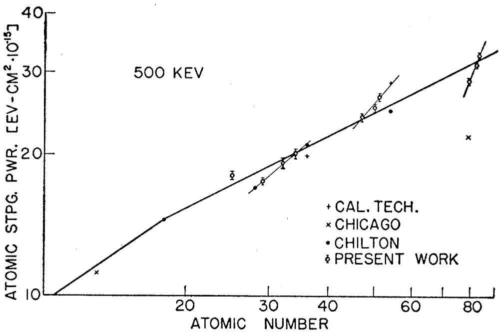


FIG. 5. The atomic stopping cross section σ as a function of atomic number, showing the relatively pronounced rise as the s and p shells are filled.

slope not much different from the line from hydrogen to argon. The same pattern is repeated starting with silver as the $5s$ and $5p$ levels are filled and again starting with gold as the $6s$ and $6p$ electrons are added. However, before too much credence can be given to this periodicity, measurements will have to be made on many more elements. It is interesting that Sternglass[16] has observed a similar periodic variation in the yield of secondary electrons as a function of atomic number when elements are bombarded with high-energy electrons. This is another phenomenon which involves the interaction between the atomic electrons and a high speed charged particle.

It should be noted that if the periodic slope changes as shown in Fig. 5 prove to be valid, then the dependence of the stopping power on the conductivity properties or upon the physical state (solid or gaseous) of an element is probably relatively small.

The authors wish to thank the other members of the Van de Graaff generator program for their help and to express their appreciation to Dr. A. B. Chilton and Professor Ward Whaling for valuable discussions. Financial support from The Ohio State University Development Fund and from the University Committee on Research Grants is gratefully acknowledged.

---

[16] E. J. Sternglass (private communication), and Phys. Rev. **80**, 925 (1950).

PHYSICAL REVIEW VOLUME 98, NUMBER 2 APRIL 15, 1955

Cosine Interaction in CsF and RbF*

G. BEMSKI,† W. A. NIERENBERG, AND H. B. SILSBEE
University of California, Berkeley, California

(Received October 7, 1954)

A series of measurements of the line shape of the fluorine resonance *versus* magnetic field have been made using a molecular-beam apparatus. Good theoretical agreement has been found for RbF. The CsF behavior is complicated by the overlapping Cs spectrum. The equivalent field at the fluorine nucleus per unit molecular rotation, H_r, is found to be 2.28 ± 0.20 gauss and 3.00 ± 0.15 gauss for RbF and CsF respectively. These results are less than those previously measured.

I. INTRODUCTION

EARLIER investigations of the fluorine resonance in the alkali fluorides resulted in discrepancies in the determination of the rotational constant c/h which is a measure of the strength of the spin-orbit coupling of the nuclear spin to the molecular rotation. The discrepancies were particularly clear for CsF and LiF. The molecular-beam magnetic-resonance apparatus (MBMR)[1] yielded 18 kc/sec for Li^{6}F^{19} compared to the value 37 kc/sec for the electrical apparatus[2] (MBER). Similarly, experiments[3] with Cs^{133}F^{19} showed values of 14 ± 2 kc/sec (strong field, MBER) or 14 ± 3 kc/sec (weak field, MBER) compared to 8 kc/sec[1] (MBMR). In addition, the curve shape of the zero field MBMR resonance for CsF did not agree with that predicted from the strong field results. It was therefore decided to repeat the CsF experiments using MBMR including measurements at intermediate fields and to perform a similar experiment using RbF with the possibility of comparison to MBER.[4]

The earlier work was carried out at either high or low fields. Since that time a theory[5] has been constructed which predicts the shape of the resonance for all values of the magnetic field in terms of just one parameter. It was hoped that some clue to the discrepancies might be found in the transition from the extreme Zeeman to the complete Paschen-Back conditions. In addition, the verification of the theory has its own intrinsic interest.

II. EXPERIMENTAL DETAILS

Since this experiment was the first to be completed using the new molecular beam apparatus at Berkeley, a brief description of the apparatus will be attempted.

---

* This research has been supported by the Office of Naval Research.

† Now at the Bell Laboratories, Murray Hill, N. J.

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

[2] J. C. Swartz and J. W. Trischka, Phys. Rev. **86**, 606 (1952).

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

[4] V. Hughes and L. Grabner, Phys. Rev. **79**, 314 (1950).

[5] W. A. Nierenberg, Phys. Rev. **82**, 932 (1951).

The apparatus is similar to its predecessors at Columbia and Harvard and was operated in a conventional manner for these experiments.[6,7]

The vacuum envelope was constructed of $\frac{1}{4}$-in. stainless steel, 12 in. in diameter, and 80 in. long. This provided for improved rigidity and no variation in beam intensity was observed due to instability of the can. The three magnets were machined from Armco iron, the pole tips conforming to the equipotentials of a two wire system.[8] The field gradient was 10^5 gauss/cm at a field of 12 000 gauss. The geometry was such that the deflection for an average alkali fluoride molecule due to a change in orientation of the F^{19} nucleus was approximately 0.006 in. at the detector. The oscillating fields were 28 cm long and therefore had a limiting resolution of approximately 1500 cycles/sec for the alkali fluorides. However, since the lines studied were of the order of half a megacycle per second in width, this resolution was not needed.

The data described in this article were obtained as averages of the differences of four beam readings with the oscillator off and five with the oscillator on. No significant variation in the results was noticed over a range of rf current between 2.5 and 5 amperes.

The oven slit-width, the collimator slit-width, and the detector diameter were all 0.001 in. The surface ionization detector fed a conventional DuBridge-Brown electrometer circuit employing a 5800 Victoreen electrometer tube.

III. THEORY OF THE EXPERIMENT

The usual Hamiltonian employed in describing this experimental situation is

$$\mathcal{H}=-\mu_N g_I \mathbf{I}\cdot\mathbf{H}-\mu_N g_J \mathbf{J}\cdot\mathbf{H}-c\mathbf{I}\cdot\mathbf{J}. \tag{1}$$

I is the fluorine spin in units of $\hbar$; **J** is the molecular angular momentum in units of $\hbar$; μ_N is the nuclear magneton; **H** is the applied magnetic field; c is the magnetic interaction in ergs per unit rotation of the molecule with the fluorine nucleus; g_I is the magnetic moment for fluorine in units of μ_N; g_J is the molecular magnetic moment in units of μ_N. In addition, there are similar terms for the other nucleus, a quadrupole term for the other nucleus and a dipole-dipole term between the two nuclei.

Table I. Fluroine resonance in RbF.

H gauss	ν_I Mc/sec	Peak position Mc/sec	$\frac{1}{2}$ width Mc/sec	c/ha Mc/sec	y_I
0	0.00	0.4	0.68	0.60	0.00
70	0.28	0.4	0.55	0.50	0.57
125	0.50	0.6	0.63	0.61	0.82
170	0.68	0.68	0.58	0.58	1.17
220	0.88	0.90	0.56	0.56	1.57
328	1.31	1.35	0.63	0.63	2.08
500	2.0	2.0	0.60	0.60	3.33
750	3.0	3.0	0.55	0.55	5.46
975	3.9	3.9	0.62	0.62	6.30

Average value of $c/ha=0.58$ Mc/sec.

Table II. Fluorine resonance in CsF.

H gauss	ν_I Mc/sec	Peak position Mc/sec	$\frac{1}{2}$ width Mc/sec	c/ha Mc/sec	y_I
0	0.00	...	...	...	0.00
130	0.52	0.51	0.46	0.45	1.15
165	0.66	0.66	0.60	0.60	1.10
990	3.96	3.96	0.71	0.71	5.6

High-field value of $c/ha=0.71$ Mc/sec

Both because $\bar{J}\gg 1$ and $g_J\ll g_I$ in these experiments, a very good approximation is to treat **J** as a stationary, classical vector. This implies[5] that in observing the fluorine resonance we may neglect the terms in the Hamiltonian involving the alkali nucleus. The dipole-dipole term is neglected because its contributions may be estimated as too small (~4 kc/sec) for the effects considered here. With these approximations, the predicted[5] line shape is:

$$\frac{dN}{dy}=\frac{\sqrt{\pi}}{2}\frac{y}{y_I}[\mathrm{erf}(y+y_I)-\mathrm{erf}|y-y_I|], \tag{2}$$

where

$$y=(ha/c)\nu,\quad y_I=(ha/c)\nu_I,\quad a=(\sqrt{\pi})/2\bar{J},$$

$$\mathrm{erf}(x)=(2/\sqrt{\pi})\int_0^x \exp(-\xi^2)d\xi.$$

$\bar{J}$ is the average over the Boltzmann distribution for the molecules in the oven, relating a to the molecular moment of inertia K through $a=(\hbar\sqrt{\pi})/(2\pi kKT)^{\frac{1}{2}}$. ν is the applied radiofrequency; y is therefore a dimensionless variable. ν_I is the Larmor frequency of the fluorine nucleus; y_I is therefore a dimensionless parameter. The quantity ha/c is the one parameter that determines the shape of the resonance curves for all values of the field.

The observed transitions are those due to $\Delta m_I=\pm 1$, $\Delta m_J=0$ in strong fields or $\Delta m_F=0, \pm 1$ in weak fields. Transitions $\Delta m_J=\pm 1$, $\Delta m_I=0$ are not detectable in this apparatus.

In strong fields the curve is symmetric and has a sharp peak centering on the Larmor frequency. As the field is decreased, the resonance curve becomes asymmetric and at vanishingly small fields the position of the maximum is determined by the internal interaction alone.

IV. THE EXPERIMENTAL RESULTS

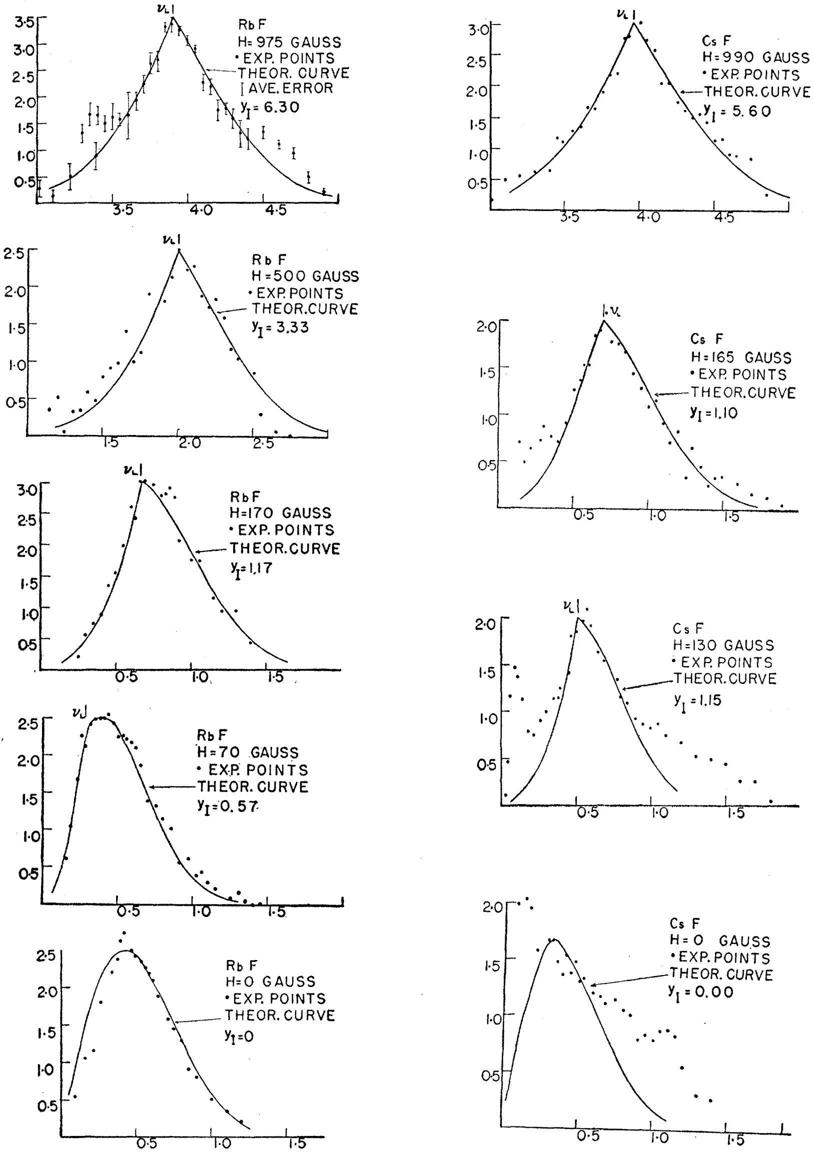
Figure 1 and Tables I and II display the data. The fluorine resonance has been observed for fields ranging

---

[6] Rabi, Millman, Kusch, and Zacharias, Phys. Rev. **55**, 728 (1939).

[7] J. B. M. Kellogg and S. Millman. Revs. Modern Phys. **18**, 323 (1946).

[8] Rabi, Kellogg, and Zacharias, Phys. Rev. **96**, 157 (1934).



(a) (b)

FIG. 1. The fluorine resonance (a) in RbF, and (b) in CsF. The ordinates are percent reduction in beam intensity; the abscissas are frequencies in megacycles per second. The solid lines are the theoretical curves; the solid points are the experimental results. The typical statistical error is shown on the RbF curve for $H=975$ gauss. Additional data for RbF at $H=750$, 328, and 125 gauss are not shown because of space limitations, but the curves are in no essential way different from the ones shown.

from strong ($H>500$ gauss, $y_I>1$), through intermediate ($300>H>100$ gauss, $y_I\sim 1$) to weak ($H<100$ gauss, $y_I<1$). Figure 1(a) shows the resonance curves for RbF *vs* magnetic field. The points are the experimental results. The solid lines are the best theoretical fits. It should be emphasized that the entire family of experimental results for the complete range of field are fitted by a theory that has but one adjustable parameter and that parameter may be estimated independently. The agreement between theory and experiment is excellent and there would seem to be little question that the assumed Hamiltonian, the theory, and the approximations made apply very well to RbF. The quantity ha/c is the only parameter for these fields and frequencies which is needed to explain these results. Unfortunately the moment of inertia of RbF is not well known. Schomacker and Stevenson's[9] method for calculating the nuclear separation yields 2.54 A for RbF. This value of r in addition to the oven temperature value of 975°K for RbF fixes $\bar{J}=56.3$.

---

[9] V. Schomacker and D. P. Stevenson, J. Am. Chem. Soc. **63**, 37 (1941).

This corresponds to a most probable $J=45.9$ which agrees with the value of 46 used by Zeiger and Bolef.[10] The average value of $c/ha=0.58$ Mc/sec combined with $a=0.0157$ results in the value $c/h=9.1\pm0.9$ kc/sec. The principal uncertainty is in the calculated r. The experimental uncertainty is less by a factor two. The related field per unit molecular rotation at the position of the fluorine nucleus $H_r=2.28\pm0.20$ gauss.

Figure 1(b) is the corresponding family of resonance curves for CsF. Here the agreement with experiment over the range of C field is poor. The line shape at very strong fields is in good agreement with theory. At intermediate and weak fields the disagreement is marked. In Sec V, most of the discrepancy is explained but as a result only the value $c/ha=0.71$ Mc/sec for strong fields can be used to evaluate c/h. The moment of inertia of CsF has been determined by Trischka[11] as $K=(152\pm6)\times10^{-40}$ g cm^2 and the corresponding nuclear separation as $r=2.36\times10^{-8}$ cm. (These values are for the first vibrational state. The values for other vibrational states differ too little to make an appreciable difference in this calculation.) As a result $\bar{J}=52.4$, $a=0.0169$, and $c/h=12.0\pm0.6$ kc/sec. The principal source of error is in the present experiments. The field H_r is 3.00 ± 0.15 gauss.

The maximum drop in beam intensity varied between 2 and 3.5 percent. This variation depends on the half-width of the beam at the detector. This, in turn, depends on the effective width of the oven slit which had a tendency to broaden with time due to "oven plugging." The CsF beam in particular gave considerable trouble and the beam was often three times wider than predicted by the geometry. The very large g factor of the fluorine nucleus was the chief reason that a sufficiently large effect was obtained. The errors in determination of c/ha are due to:

1. The actual fitting of the theoretical curve of proper half-width. A possible error of 2–3 percent is not excluded.

2. Average error in measurement of beam changes in intensity. The 975-gauss curve, Fig. 1(a), shows this vertical spread in detail.

3. Changes in magnetic field values during a run. The error on this account was less than 1 percent for $H>100$ gauss, and 2 percent for $H<100$ gauss.

4. Frequency. The frequency was measured to better than 1 percent.

5. Absolute error in C field. A flip-coil calibration checked the sharp peak of the fluorine resonance at high fields to better than 2 percent. A residual field exists for $H<200$ gauss and the field values reported have been corrected for this effect. The corrections do not affect the c/ha values.

V. DISCUSSIONS AND CONCLUSIONS

It has been previously noted (Sec. IV) that the RbF spectral curves fit the theory with excellent agreement. The result, $c/h=9.1\pm0.9$ kc/sec is less than but consistent with Hughes and Grabner's[4] result of 12 ± 3 kc/sec. (This number is obtained by taking the weighted average of 11 ± 3 for Rb^{85}F and 14 ± 3 for Rb^{87}F.) These measurements were made at Columbia on the electric molecular apparatus by using low rotational states. At first glance the agreement with theory is surprising inasmuch as the Rb resonance could be expected to confuse the pattern. However, this resonance has been extensively investigated by Zeiger and Bolef.[10] At zero magnetic field the maximum observable resonance due to the Rb^{87} is confined to the region 8.0−8.6 Mc/sec and has a peak intensity of 0.2 percent due to the large quadrupole moment. The F resonance at zero field is confined to the region 0.0−1.5 Mc/sec and has a peak intensity of 2.6 percent. Therefore the Rb^{87} spectrum is ineffectual at zero field for two reasons. At higher fields where the two spectra may overlap, the Rb^{87} intensity is reduced even further by the Zeeman spreading but the F resonance intensity is essentially unchanged. Zeiger and Bolef never observed the Rb^{85} resonance, presumably because the peak intensity was considerably less than 0.2 percent. This result has a sound theoretical basis.

The CsF strong field result $c/h=12.0\pm0.6$ kc/sec must be compared with Trischka's[11] results for strong and weak fields of 18 ± 2 and 14 ± 3 kc/sec respectively. The agreement with the average, 16 ± 3 kc/sec is poor and the deviation is in the same direction. The poor agreement of the line shape at intermediate and weak fields [Fig. 1(b)] has been tentatively assigned to the Cs resonance. The measured[11] $e^2qQ/h=0.62$ Mc/sec. Cs has a spin of 7/2. Under these circumstances Feld and Lamb[12] predict zero-field quadrupole peaks at 0.0444, 0.0888, and 0.1332 Mc/sec. These peaks are sufficient to explain the anomalous behavior of the low-frequency side of the F resonance. The departure from the high-frequency side of the F resonance is not understood.

---

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

[11] J. W. Trischka, Phys. Rev. **74**, 418 (1948).

[12] B. T. Feld and W. E. Lamb, Jr., Phys. Rev. **67**, 15 (1945).