If the granite, protected from cosmic rays by thick layers of rock, shows the same ionizing effect as in the laboratory, we will have to assume that a hitherto unknown penetrating radiation is given off by the granite itself. It will be interesting to investigate other volcanic rocks of different uranium and thorium content in order to see whether this effect is correlated with the content of radioactive materials in the rocks.

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Grateful acknowledgment is also given to Dr. L. J. Adams, Dr. W. D. Urry, and Dr. W. Davis of the Geophysical Laboratory (Carnegie Institution of Washington, D. C.), Dr. M. A. Tuve, Department of Terrestrial Magnetism (Carnegie Institution of Washington, D. C.), and Dr. L. F. Curtiss (National Bureau of Standards) for their helpful cooperation.

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The Electric Resonance Method of Radiofrequency Spectroscopy The Moment of Inertia and Electric Dipole Moment of CsF*

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This paper describes a new method of radiofrequency spectroscopy in which transitions between the energy levels of a single rotational state of a linear rotator in an electric field are caused by a superimposed radiofrequency field. The method utilizes a molecular beam and has been applied to the measurement of the moment of inertia, I, and the electric dipole moment, μ, of CsF. Values for these quantities are: $I=(187\pm22)10^{-40}$ g cm^2 and $\mu=7.3\pm0.5$ Debye. The internuclear distance, derived from the moment of inertia, is 2.60 ± 0.16 angstroms.

1. INTRODUCTION

THE purpose of this paper is to describe some experiments[1] on CsF, a linear polar molecule which is convenient to handle, in which the molecular beam resonance method was applied to molecules in a single rotational state and in which the fields were all electric instead of magnetic. With the demonstrated high resolving power of this method, it is possible to evaluate the parameters which enter into the orientation polarizability of a molecule, namely, the moment of inertia and the electric dipole moment. In addition, it is expected that the resolving power will be so high that the variation of these quantities with vibrational quantum number will be observed. From the standpoint of nuclear physics it is also interesting that the resolving power should be ample to measure accurately the interaction of the nuclear electric quadrupole moment[2] with the electric field gradient of the electrons, and the interaction of the nuclear magnetic moment with the rotation of the molecule. These latter points will be developed in another paper from this laboratory.

The molecular transitions which have been observed are not of the ΔR type (transitions between different rotational states) since the microwave techniques required for their observation were not developed at the time that the apparatus was designed.[3] Rather, the transitions are between states with the same value of R but

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** Now at Socony-Vacuum Laboratories, Brooklyn, New York.

[1] H. Hughes, Phys. Rev. **70**, 570 and 909 (1946).

[2] Dr. U. Fano, National Bureau of Standards, private communication.

[3] Recently Dakin, Good, and Coles, Phys. Rev. **70**, 560 (1946), have observed a ΔR-type transition of OCS in a wave guide at 24,320 Mc. The frequency for the $R=1\rightarrow R=0$ transition of CsF is 8830 Mc. This is a wave-length of 3.4 cm.

different values of p, the electric quantum number. One can thus study the molecular transitions at frequencies in the ordinary radiofrequency range, and it is not necessary to stabilize a microwave oscillator in order to measure the small frequency differences which arise from the fine structure.

Shortly after the molecular beam technique was developed by Stern and others, it was applied to the measurement of electric moments. These moments were evaluated from deflection experiments[4–8] in which the transverse displacement of a beam of molecules depended upon their velocity, mass, effective electric moment, the deflecting field, and the geometry of the apparatus. Because of the distribution of velocities and effective electric moments in the beam, the field broadened the beam, the center deflected only a trifle, and the values of μ which were obtained by this method were only approximate.

The electric resonance method differs markedly from deflection experiments, since it is not necessary to evaluate the distribution of velocities, to calibrate the deflecting field, or to assume a constant intensity of the beam. In addition, the moment of inertia is obtained as well as the electric dipole moment. Experiments designed to measure the moment of inertia and the distortion polarizability by the deflection method have not been reported, though in principle they are possible. It is unlikely that the results would be very precise.

In the molecular beam electric resonance method transitions are induced between energy levels of a linear rotator in an *electric* field by a superimposed radiofrequency electric field. From a knowledge of the d.c. field and the frequency at which the transition occurs, one can compute the electric moment, μ, and the moment of inertia, I.

The first molecule to which this method was applied was cesium fluoride, because it is readily handled by standard molecular beam methods and its spectrum has no isotope effects. Another attractive property is its low moment of inertia compared with other alkali halides. This simplifies the intensity problem for reasons described below.

This method is closely analogous to the magnetic resonance method[9] which has been applied previously to atoms and molecules. It is an advance over previous methods in that a single rotational state of the molecule is studied even though it is present to only one part in ten thousand as a component of the beam.

While the theory and techniques presented in this paper relate only to linear molecules, it would appear a fruitful undertaking to examine the broad field of electric resonances in non-linear molecules. For these there is a first-order Stark effect and such molecules should be easier to deflect. The theory, however, will probably be considerably more complicated than that for linear molecules.

Definitions of the symbols are given in Table I.

2. METHOD

The beam of molecules can be formed and detected by any of the well-known molecular beam techniques. In this case the CsF molecules evaporate from a hot oven, are collimated by slits, and pass through two inhomogeneous electric fields which refocus one, or at most two, rotational states upon a surface ionization detector. Between these two fields is a short homogeneous electric field upon which is superimposed a radiofrequency electric field at right angles to the d.c. field. Here molecules may undergo transitions between different energy levels.

TABLE I. Definitions of letter symbols.

A_{R,p^2}	$[(R+1)^2-p^2]/(2R+1)(2R+3)$
E	Electric field strength in volts per cm except where stated otherwise
f	Frequency in cycles per second
I	Moment of inertia in g cm^2
p	Electric quantum number
R	Rotational quantum number
V	Electric potential difference
W	Energy
ϵ	$W/(\hbar^2/2I)$
λ	$\mu E/(\hbar^2/2I)$
μ	Permanent electric moment in e.s.u.
μ_e	Effective electric moment $(=-\partial W/\partial E)$, in e.s.u.

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[4] For a general discussion of the field, see R. G. J. Fraser, *Molecular Beams* (Chemical Publishing Company, New York, 1938) and R. G. J. Fraser, *Molecular Rays* (The Macmillan Company, New York, 1931).

[5] Erwin Wrede, Zeits. f. Physik **44**, 261 (1927).

[6] Max Wohlwill, Zeits. f. Physik **80**, 67 (1932).

[7] H. Scheffers, Physik. Zeits. **41**, 89 and 98 (1940); Rodebush, Murray, and Bixler, J. Chem. Phys. **4**, 372 (1936).

[8] Estermann, Zeits f. physik. Chemie B**1**, 161 (1928) and **2**, 287 (1929); Leipziger Vorträge (1929), pp. 17 ff.

[9] Rabi, Millman, Kusch, and Zacharias, Phys. Rev. **55**, 526 (1939).

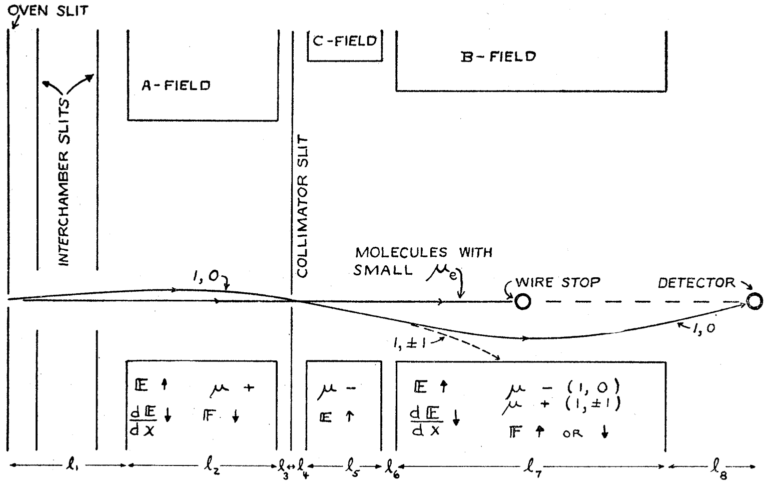

FIG. 1. Schematic diagram of the apparatus and paths of the molecules.

The selection of the particular electric state for study is accomplished by two inhomogeneous electric fields, named the A- and B-fields, which together cause molecules in the desired state to follow a sigmoid path around a wire stop and to fall upon the detector, as is shown in Fig. 1. Figure 2 shows the energy levels of a rotating polar linear molecule in an electric field. Only those molecules are refocused for which the electric moment has the correct sign and magnitude in the two fields. As shown in Fig. 3, at low fields molecules in state (1, 0) have a negative moment, while at high fields their moment is positive. If, then, $\mathbf{E}$ and $d\mathbf{E}/dx$ point in the same direction in both the A- and B-fields, and if the values of λ_A and λ_B are, respectively, greater and less than about 5 (at which $\mu_e=0$), (1, 0) molecules (and also some (2, ±1) molecules) will be refocused, but all others will hit either the wire stop or some other part of the apparatus. This is diagrammed in Fig. 1 where also are shown the directions of the various vectors and the signs of μ_e in all three fields. There are (1, 0) molecules streaming from the oven in all directions, but only those are refocused which start with just the correct angle.

The detected beam shows a decrease when the frequency of the oscillating field equals the difference in the energy of the two levels divided by Planck's constant. For CsF, transitions involving changes in the electric quantum number, p, are possible in the radiofrequency region in the presence of a static electric field. The rotational spectrum, for which the rotational quantum number changes, lies in the microwave region[3] and was not investigated. The matrix element for electric dipole radiation of the $\Delta R=0$, $\Delta p=\pm 1$ type is different from zero only when the constant homogeneous field and the oscillating field are at right angles.

To reduce the general background against which these transitions are observed, a wire stop is placed in the path of the beam and the molecules in the beam are refocused around it.

Zero Moments

In this experiment, $\mu^2 I$ is calculated from the frequency and the field for a Δp transition (constant R), while by observing the departure of the frequency from a quadratic dependence on the field, it is possible to obtain a value of μI. By combining these two values, it is thus possible to obtain μ and I separately. The value of μI may also be obtained by the zero-moment method which, in analogous magnetic experiments, was used so often prior to the development of radiofrequency spectroscopy. All rotational states beyond $R=0$ possess at least one zero moment, two of which appear clearly in Fig. 3. For example, the 1, 0 state effective electric moment is zero near $\lambda=5$, while the 2, ±1 moment is zero at about $\lambda=5.6$. It is relatively simple to locate these points, and this experiment was done in order to establish the values of μ and I in a preliminary fashion. The precision of the final result depends upon a knowledge of the deflecting field, E, at the exact position of the beam, a quantity which is somewhat difficult to obtain. The line-up of the beam changes as the oven is heated, yet values determined optically while the can is open must be used. Better values of the deflecting field E can be obtained by observing the effect of a calibrated shift of the oven, the collimator slit, and the detector, but this technique has not been perfected. Clearly, the electric resonance method is superior to the zero-moment method.

3. THEORY

Energy Levels of a Linear Rotator

The solution to Schroedinger's equation for the energy levels of a linear, rigid rotator in an electric field is generally obtained by the perturbation method from the well-known solution for the zero-field case. Because there is no time-average electric moment in a zero field, the first-order perturbation term is zero. Kronig[10] and others have given the second-order solution as follows:

$$W=\frac{\hbar^2}{2I}\left[R(R+1)+\tfrac{1}{2}\lambda^2\left\{\frac{R(R+1)-3p^2}{R(R+1)(2R-1)(2R+3)}\right\}\right]. \qquad (1)$$

This equation gives the oscillator frequency for a transition by application of the usual Bohr relation. It is customary to designate the stationary states by two numbers which give the rotational and electric quantum numbers. For the (1,0)→(1, ±1) and the (2, ±1)→(2, ±2) transitions observed in this experiment, Eq. (1) yields Eqs. (19) and (20) below.

The next non-zero perturbation term is the fourth which Brouwer[11] found and, since his thesis is not readily available in the United States, his Eqs. (2) through (7) for the first three rotational states are reproduced below. By the use of the parameters λ and ϵ, generalized equations are obtained which are independent of the particular values of μ and I of any single molecule.

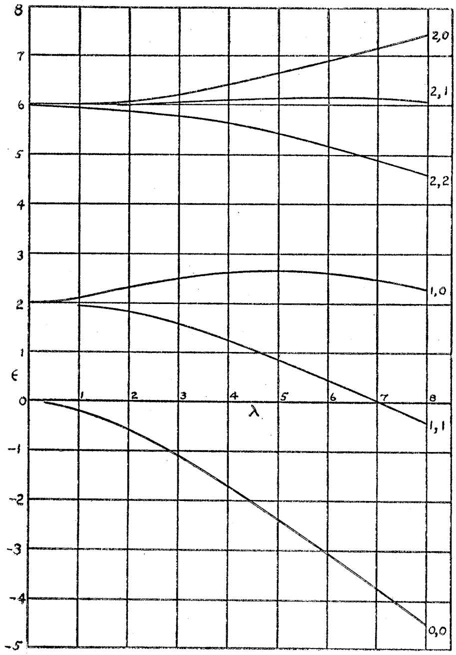

FIG. 2. Energy levels of a rotating polar linear molecule in an electric field.

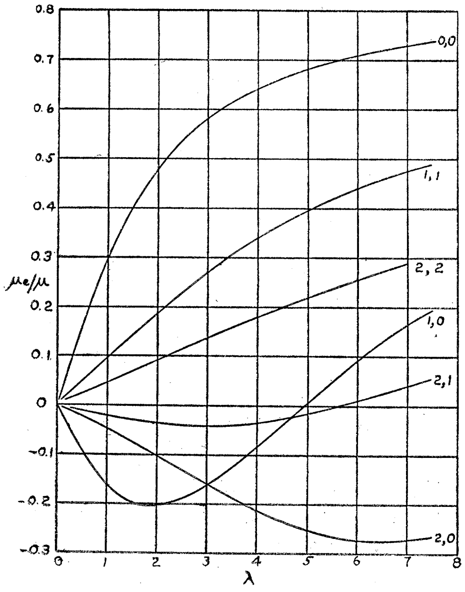

FIG. 3. Effective electric moments of a rotating polar linear molecule in an electric field.

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[10] Kronig, Proc. Nat. Acad. Wash. 12, 608 (1926).

[11] F. Brouwer, Dissertation, Amsterdam, 1930.

$R=0,\ p=0$:

$$\epsilon=-\frac{1}{6}\lambda^2+\frac{11}{1080}\lambda^4-\frac{1}{725}\lambda^6+\cdots, \tag{2}$$

$R=1,\ p=0$:

$$\epsilon=2+\frac{1}{10}\lambda^2-\frac{73}{7900}\lambda^4+\cdots, \tag{3}$$

$R=1,\ p=\pm 1$:

$$\epsilon=2-\frac{1}{20}\lambda^2+\frac{19}{56{,}000}\lambda^4+\cdots, \tag{4}$$

$R=2,\ p=0$:

$$\epsilon=6+\frac{1}{42}\lambda^2+\left(\sim\frac{1}{3000}\right)\lambda^4+\cdots, \tag{5}$$

$R=2,\ p=\pm 1$:

$$\epsilon=6+\frac{1}{84}\lambda^2-\frac{1}{3000}\lambda^4+\cdots, \tag{6}$$

$R=2,\ p=\pm 2$:

$$\epsilon=6-\frac{1}{42}\lambda^2+\left(\frac{1}{25{,}000}\right)\lambda^4+\cdots. \tag{7}$$

The value of λ to which these equations are useful is determined by the desired accuracy and may be found by comparison with Lamb's exact Eq. (18) below. At $\lambda=1$ for the $1,0\rightarrow 1,\ \pm 1$ transition, the two equations agree to better than 0.1 percent.

Fraction of Molecules Available

As calculated from the partition function, the fraction of molecules in the state $R=1$ is

$$\sigma_1=N_1/N=3(h^2/2I)/kT. \tag{8}$$

The fraction of molecules in the $R=0$ state, σ_0, is $\frac{1}{3}$ of σ_1. For purposes of exploring the electric resonance method where the amount of refocused beam is an important consideration, it is obviously desirable to work with a high value of σ_1 and hence to employ molecules with a low value of I. Substituting the known values of the constants (see Section 6 below), we find that

$$\sigma_0=0.21/T, \tag{9}$$

$$\sigma_1=0.63/T. \tag{10}$$

Since the first rotational level is threefold degenerate and the fields are only 50 percent effective in selecting the desired molecules, this experiment has been performed with only about one ten-thousandth of the total beam.

Transition Probability

At zero field, a Δp transition in which $\Delta R=0$ is forbidden, but this selection rule is broken by the constant field, and both theory and experiment show that only a small field is needed to induce the $(1,0)\rightarrow(1,\pm 1)$ change. A negligible amount of power is required, and even a small oscillator is adequate, provided only that its output is a few volts.

The optimum condition for producing a transition is

$$M\tau\sim h, \tag{11}$$

where τ is the transit time of the molecule in the C-field and the matrix element, M, is given by

$$M=\int_V \psi_{1,0}{}^*E_{\mathrm{rf}}\mu_e\psi_{1,\pm 1}dV. \tag{12}$$

E_{rf} is $\frac{1}{2}$ of the peak value of the perturbing r-f field, and the ψ's are the perturbed wave functions. This matrix element has been calculated using the wave functions for a rotating dipole, and the final result is

$$M=\frac{\mu^2E_{\mathrm{rf}}E_{\mathrm{dc}}3\sqrt{2}}{40(h^2/2I)}. \tag{13}$$

On substituting the equation for the frequency of this transition

$$f=\frac{3\mu^2E_{\mathrm{dc}}{}^2}{20h(h^2/2I)}. \tag{14}$$

Eq. (13) simplifies to

$$E_{\mathrm{rf}}/E_{\mathrm{dc}}\sim\sqrt{2}/2\pi\tau f\doteq 1/4.5\tau f. \tag{15}$$

The transit time τ is of the order of 10^{-4} seconds, so that the theoretical ratio of the r-f field to the d.c. field is much less than unity for all frequencies in the megacycle range.

For an ideally uniform C-field, the probability of a transition, P, is related to this same ratio and to the ratio of the frequency f and the resonance frequency f_0 by the relation[12]

$$P=\frac{0.5}{1+(E_{\mathrm{dc}}/E_{\mathrm{rms}})^2(1-f/f_0)^2}. \qquad (16)$$

This relation takes into account the v^3-type velocity distribution of molecules in the beam.

For a $\Delta p=\pm 1$ transition, the oscillating field must be perpendicular to the d.c. field. When they are parallel, Δp must be equal to 0.

4. APPARATUS

General

The broad features of the apparatus are similar to those previously described[9] for the magnetic resonance method. The outer envelope of the apparatus is a 7-in. O.D. brass pipe, $24\frac{11}{16}$ in. long, crossed by an $8\frac{3}{4}$-in. O.D. brass pipe of length $10\frac{1}{2}$ in. The cross pipe provided convenient access to the fields. The apparatus is divided into three chambers by two plates on which are mounted slits just large enough to pass the beam. Each chamber is pumped separately. The first contains the oven, the second or "interchamber" isolates the oven chamber with its relatively poor vacuum ($\sim 10^{-5}$ mm Hg) from the third or "observation" chamber ($p<10^{-6}$ mm Hg) which contains all the fields and the detector. There are liquid nitrogen traps in all chambers.

In traveling to the surface ionization detector approximately 50 cm from the oven slit, a molecule passes first through a 10-cm inhomogeneous electric field (*A*-field), then through a 5-cm homogeneous electric field on which is superimposed a radiofrequency field normal to the d.c. component (*C*-field), and finally through another inhomogeneous field (*B*-field), 18 cm long, in which is placed the stop wire previously mentioned. The stop is 0.023 cm in diameter. Its function is described further below. Figure 1 depicts schematically the trajectory of molecules which are refocused and molecules which hit the stop.

Oven

The beam is produced by evaporation of CsF molecules in an iron oven heated to about 575°C and collimated by slits to a height of 0.3 cm and a width of 0.0075 cm. The oven, approximately a one-inch cube, is heated by coils of 0.010-in. tungsten wire which are insulated from the oven by short lengths of quartz tubing. As the oven gassing increases with temperature, a best "signal-to-noise" ratio was found, at 850°K. At this temperature $\sigma_0=0.00025$, $\sigma_1=0.00074$, and there are 200 rotational states populated up to the point where the Boltzmann exponent equals one.

A- and *B*-Fields

As previously described, the function of the deflecting fields is to select certain of the molecules for study. The general method of accomplishing this is well known.[4]

To apply the equations for the deflection of a molecule in an inhomogeneous field, it is necessary to know the force, F, in the direction, s. This is, in general,

$$F_s=\mu_e \partial E/\partial s. \qquad (17)$$

TABLE II. The energy levels of a rotating polar linear molecule as a function of the electric field strength, calculated from Lamb's equation, and the effective electric moment calculated by first differences. $\mu_e/\mu=-d\epsilon/d\lambda$.

λ	ϵ	μ_e/μ	ϵ	μ_e/μ	ϵ	μ_e/μ
	$(R=0,\ p=0)$		$(R=1,\ p=0)$		$(R=1,\ p=1)$	
0.0	0.00000	0.000	2.000000	0.000	2.000000	0.000
0.5		+0.158		−0.091		+0.050
1.0	−0.15766		2.090758		1.95033	
1.5		0.400		−0.196		0.145
2.0	−0.55728		2.287173		1.805104	
2.5		0.535		−0.191		0.231
3.0	−1.09266		2.477962		1.57410	
3.5		0.612		−0.124		0.304
4.0	−1.70485		2.602378		1.26985	
4.5		0.661		−0.036		0.365
5.0	−2.36560		2.638730		0.904751	
5.5		0.695		+0.051		0.415
6.0	−3.06022		2.587276		0.48954	
6.5		0.720		+0.129		0.457
7.0	−3.78014		2.458169		+0.032949	
7.5		0.740		+0.194		0.491
8.0	−4.51990		2.263945		−0.458136	
	$(R=2,\ p=0)$		$(R=2,\ p=1)$		$(R=2,\ p=2)$	
0.0	6.000000	0.000	6.000000	0.000	6.00000	0.0000
0.5		−0.024		−0.012		+0.0238
1.0	6.024033		6.011578		5.97623	
1.5		−0.074		−0.031		0.0708
2.0	6.098452		6.042636		5.90540	
2.5		−0.129		−0.041		
3.0	6.227791		6.083712			0.138
3.5		−0.185		−0.039		
4.0	6.412842		6.122985		5.62877	
4.5		−0.233		−0.026		
5.0	6.645478		6.149323			0.220
5.5		−0.263		−0.005		
6.0	6.908774		6.153928		5.18863	
6.5		−0.273		+0.023		
7.0	7.181753		6.130768			0.290
7.5		−0.263		0.054		
8.0	7.444437		6.076336		4.60850	
8.5				0.087		
9.0			5.989152			

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[12] Dr. Willis Lamb, private communication.

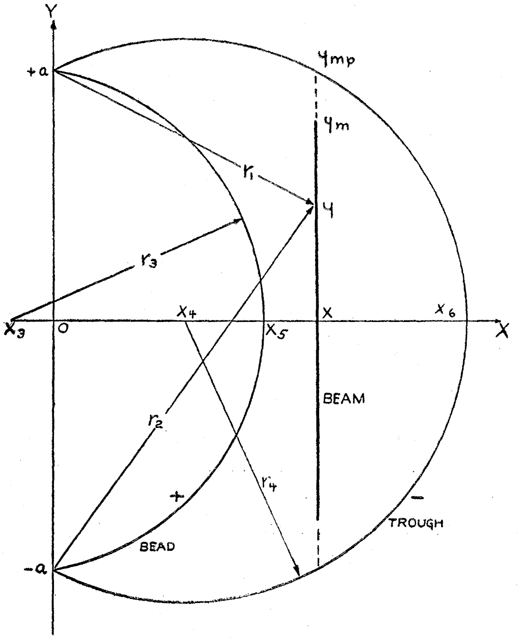

FIG. 4. Cross section of the A-field as viewed from the detector.

E and $\partial E/\partial s$ are well known[13, 14] for the type of field used. μ_e is not a constant but must be calculated from the energy by differentiation. In this experiment, the deflecting field E is so large that the energy cannot be calculated from the perturbation solutions to Schroedinger's equation given above but must be derived from the exact solution. This yields a three-term recursion formula, and the energy eigenvalues are best determined through the continued fraction method.[12] The values of the parameter ϵ listed in Table II were determined by successive approximations in the implicit Eq. (18).

$$\epsilon = p(p+1) - \frac{\lambda^2 A_{p,\,p}{}^2}{(p+1)(p+2)-\epsilon-\dfrac{\lambda^2 A^2{}_{p+1,\,p}}{(p+2)(p+3)-\epsilon-\text{etc.}}}. \quad (18)$$

This equation neglects the distortion polarizability of the molecule,[4] which is quite small, the magnetic moments of the nuclei, and the quadrupole moment of the cesium nucleus. Fluorine with a spin of ½ is not expected to possess a nuclear quadrupole moment.

To maintain the resolution of the apparatus, the beam should not spread or warp as it passes through the deflecting fields, and consequently F should be as constant as possible over the beam. As Eq. (17) shows, this does not mean that the gradient of the field should be constant. Figure 4 is a cross section of the field which meets these requirements. It consists of parts of two cylindrical surfaces with parallel axes. The design constants of the deflecting fields are listed in Table III.

Two independent half-wave rectifiers supply the A- and B-fields. Even with voltmeters connected, the output current is very small so that R-C filters provide excellent direct current. Small neon transformers with the primaries connected to 10,000-ohm potentiometers and the secondaries to 879's are used. Power is taken from the same Raytheon voltage regulator which supplies the oven. All three electric fields point in the same direction in order to maintain the quantization unchanged in the absence of a transition. This is essential to good refocusing. For the same reason, the collimating slit is quartz, not metal.

C-Field

One of the C-field plates is split horizontally. One of the halves is grounded while the other is

TABLE III. Design constants of the A- and B-fields.

Quantity	A-field	B-field	Units
x/a	1.05	1.50	—
y_m/a	0.8	1.2	—
λ	~6.6	~2.0	—
R	2.0	3.5	cm^{-1}
E	~8000	~2400	v/cm
dE/dx	~16,000	~8400	v/cm^2
$s_{\alpha b10}$		0.012	cm
a	0.500	0.264	cm
y_m	0.400	0.317	cm
x	0.525	0.396	cm
y_{mp}/a	1.0	1.5	—
y_{mp}	0.500	0.396	cm
Good to	1.5	2.0	%
l	10.0	18.0	cm
r_3	0.507	0.266	cm
x_3	−0.082	0.030	cm
r_4	0.565	0.406	cm
x_4	0.263	0.308	cm
Gap	0.402	0.418	cm
V_4	~2500	~770	v
$-F_A/F_B$	1.27	1.27	—
$x-x_5$	0.1	0.1	cm
μ_e	~+0.10	~−0.15	debye

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[13] Sidney Millman, Phys. Rev. **47**, 739 (1935).

[14] Rabi, Kellogg, and Zacharias, Phys. Rev. **46**, 157 (1934).

connected to a tap on the tank coil which is at d.c. ground potential. The other C-field plate is at r-f ground but at a d.c. potential which can be varied by means of potentiometers. The gap is somewhat under 5 mm. In parallel with the potentiometers is a Leeds and Northrup voltage divider connected to a Type K-3 Leeds and Northrup potentiometer. The C-field gap was measured accurately on a dividing engine.

The r-f source is a Hartley oscillator, parallel fed, with the tank at d.c. ground.

Wire Stop

Hanging from an extension of a ground joint in the top of the apparatus and passing through the slot in the B-field is a 0.009-in. wire. This stops all molecules of low effective electric moment which are not subject to the refocusing operations. It can be moved under vacuum and is damped by an eddy-current copper plate hanging between four U-shaped Alnico magnets. About 50 percent of the (1,0) molecules get around the stop and hit the detector.

Detector

The beam falls on a 0.003-in. tungsten wire exactly in line with the oven and collimator slits and maintained at approximately 475°C by a current of from 260 to 280 ma. After evaporating, the ionized molecules are attracted to a near-by negative plate and the current amplified by an FP-54 tube feeding a galvanometer. To clean the detector wire, it is flashed for two seconds at approximately 950°C by a current of 700 ma.

Constants of the Apparatus

Other important dimensions of the apparatus which have not previously been given follow. All dimensions are in cm.

$l_1=8$ $l_5=5$ start of B-field to stop $=8.72$
$l_2=10$ $l_6=1$ total beam $=50$
$l_3=1$ $l_7=18$ slits $=0.0075$
$l_4=1$ $l_8=6$

These distances are shown in Fig. 1.

5. PROCEDURE

With the end plates off, the oven slit, collimator slit, and detector are aligned optically using a telescope with a micrometer microscope head. The system is then pumped down and the final alignment made with the beam as indicator. A typical value for the beam during a run is 50,000 cm of galvanometer deflection. After the stop is centered the galvanometer deflection is about 7 cm which is a residual beam of 0.015 percent; this is caused by scattering. The B-field is then turned on and the A-field adjusted for a maximum refocused beam. This is about 10 cm of which an estimated 6 cm is in the (1,0) state and the remaining in the (2, ±1) state. This actual fraction of the beam in the useful (1,0) state, 0.00012, is to be compared with the partition-function value calculated with Eq. (10) above, $\sigma_1/3=0.00025$. As a means of selecting the (1,0) state, the fields are thus about 50 percent effective.

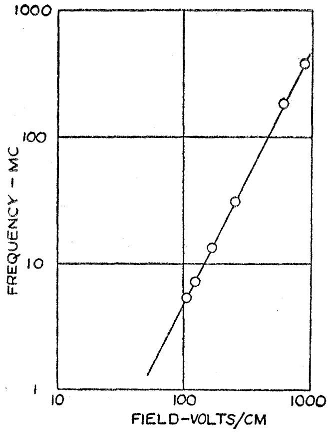

FIG. 5. Plot of frequency *vs.* field for the $(1,0)\rightarrow(1, \pm 1)$ transition of CsF.

From 10 cm of refocused beam in a typical run, 4 cm undergo transitions from the (1,0) state and 3 cm from the (2, ±1) state. This is an actual transition probability of 70 percent at resonance. These are only approximate figures, for the background may be a function of the field.

Identification of Transitions

The $(1,0)\rightarrow(1, \pm 1)$ transition was picked up first in a sweep of the C-field at fixed frequency. Complete identification could not be made merely by establishing a quadratic relationship between the frequency and the field. From the values of the A- and B-fields, it was fairly certain that only three transitions could be observed. These were: (1,0)→(1, ±1), (2, ±1)→(2,0), and (2, ±1)→(2, ±2). In a further sweep of the C-field, a transition with a different value of f/E^2 was found and, by comparing the ratios of these two values of f/E^2 with the theoretical values which may be derived from Eq. (1), the identity of both of the transitions was established unambiguously.

6. RESULTS

Figure 5 shows the frequency *vs.* field plot for the (1,0)→(1, ±1) transitions on log-log coordinates. The equations for the (1,0)→(1, ±1) and the (2, ±1)→(2, ±2) transitions are:

$$(1,0)\rightarrow(1,\pm1)\quad f=\frac{3\mu^2IE^2}{10\hbar^2h(300)^2}=448E^2,\tag{19}$$

$$(2,\pm1)\rightarrow(2,\pm2)\quad f=\frac{3\mu^2IE^2}{42\hbar^2h(300)^2}=107E^2.\tag{20}$$

Here f is in cycles per second and E in volts per cm. For CsF, $\mu^2I=9.89\cdot10^{-73}\pm1.2$ percent electrostatic units.

At low C-fields, the frequency, f, is proportional to the square of the field, E. At higher fields there is an important deviation from this quadratic relation which permits the separate determination of μ and I. Subtracting Eqs. (3) and (4), we find for the (1,0)→(1, ±1) transition frequency:

$$f=\frac{3\mu^2E_{\text{e.s.u.}}{}^2}{20h(\hbar^2/2I)}-\frac{0.00959\mu^4E_{\text{e.s.u.}}{}^4}{h(\hbar^2/2I)^3},\tag{21}$$

where E is in e.s.u.'s. Let us define two experimentally determined constants, α and β, by the relation

$$f/E^2=\alpha-\beta E^2,\tag{22}$$

where E is in volts per cm. Then

$$\alpha=\frac{3\mu^2}{20h(\hbar^2/2I)(300)^2},\tag{23}$$

$$\beta=\frac{0.00959\mu^4}{(300)^4h(\hbar^2/2I)^3},\tag{24}$$

$$I=\frac{9\beta\hbar}{2\pi800(0.00959)\alpha^2}=(1.97)10^{-28}\frac{\beta}{\alpha^2},\tag{25}$$

$$\mu^2=\frac{8(0.00959)10^7h^2\alpha^3}{3\beta}=(1.12)10^{-47}\frac{\alpha^3}{\beta}.\tag{26}$$

It is interesting to note from Eqs. (22) and (25) that the value of E does not enter into the calculation of I but only into μ.

A least-square analysis of the data was made assuming the validity of Eq. (22). The following values were obtained for the two experimental constants: $\alpha=448\pm5.4$ and $\beta=(1.91\pm0.23)10^{-5}$. Even at 500 Mc the deviation from the quadratic relation is still very small so that a small error in f/E^2 causes a large error in β. The error in f/E^2 is a function of the width of the resonance curve and this, in turn, depends in part upon the homogeneity of the C-field. The present limitation in the accuracy with which β can be measured is largely instrumental and can be eliminated. The method is capable, therefore, of yielding very good results.

Inserting the values for α and β in Eqs. (25) and (26) we obtain: $I=(187\pm22)10^{-40}$ g cm^2 and $\mu=7.3\pm0.5$ Debye. A Debye is 10^{-18} e.s.u. From the value of I, we may calculate the internuclear distance, r, as 2.60 ± 0.16 angstroms. In m.k.s. units, the values of these quantities are: $I=(187\pm22)10^{-47}$ kg m^2, $\mu=(2.4\pm0.2)10^{-29}$ coul-m and $r=(2.60\pm0.16)10^{-10}$ m.

For CsF the parameter λ is related to the field by the equation

$$\lambda=(8.3)10^{-4}E,\tag{27}$$

where E is in volts/cm. The quantity $(\hbar^2/2I)$ which occurs frequently in the theory is equal to (2.92) 10^{-17} g cm^2 sec.$^{-2}$. The rotational constant, B, is:

$$B=(1/hc)(\hbar^2/2I)=0.147\text{ cm}^{-1}.\tag{28}$$

7. DISCUSSION

As a means of making a preliminary estimate of I, one can use the observed internuclear distance obtained from x-ray diffraction data for crystals and assume some reasonable percentage reduction in going over to the gaseous state. Various tables of x-ray crystallographic data exist[15] while Herzberg[16] gives an excellent table

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[15] See for example Albright, *Handbook of Chemistry and Physics* (Chemical Rubber Publishing Company, Cleveland, 1942), 26 ed., p. 1911.

[16] Gerhard Herzberg, *Molecular Spectra and Molecular Structure* (Prentice-Hall, Inc., New York, 1939), p. 482.

of molecular constants for gases derived from band spectra which is complete as of July of 1939. CsF is not listed, but the percent reduction for similar molecules can be calculated. In a private communication, Professor Gerhard Herzberg very kindly estimated the internuclear distance by this method as 2.68A. If one uses the average reduction of 14 percent found by Maxwell, Hendricks, and Mosley[17] for other Cs compounds then $r=2.58$A.

Some years ago, Pauling[18] and others introduced the idea of ionic radii of atoms, the simple addition of which yields the internuclear distance for a wide variety of compounds in the solid state. The values for Cs and F are, respectively, 1.65 to 1.69 and 1.33 to 1.36. These total 2.98 to 3.05 which is in excellent agreement with the observed value of 3.00A. Later Pauling extended this method to gases. The most recent values are in a paper by Schomaker and Stevenson[19] who give the following equation:

$$r_{AB}=r_A+r_B-0.09|X_A-X_B| \tag{29}$$

in which the sum of the covalent radii of the two atomic species is reduced by a fraction of the absolute difference of their "electronegativities."[20] The authors list the following values for Cs and F: $r_{\mathrm{Cs}}=2.25$, $r_{\mathrm{F}}=0.72$, $X_{\mathrm{Cs}}=0.7$ and $X_{\mathrm{F}}=4.0$. In a private communication, Professor Charles P. Smyth very kindly calculated r for CsF by this method as 2.67A. Other theoretical calculations by Rice[21] vary between 2.60 and 2.66A.

Less is known concerning the distribution of charge around the molecule than about the internuclear distance, and so theoretical values for μ are still in a rudimentary state. Hannay and Smyth[22] define a term which they call the "amount of ionic character" as (μ/re) and Professor Smyth in a letter has estimated this as 0.91 and $\mu=11.6$ Debye. He stated that the error might be at least 10 percent and μ was more likely to be high than low. The observed value reported here is 7.3 ± 0.5 Debye which is an "amount of ionic character" of only 59 percent. Since CsF has the greatest electronegativity difference of any possible pair of elements, barring 87, an accurate value for μ is obviously of interest in establishing the values of the electronegativities of the elements since these vary in a regular manner through the periodic table.

The advent of the electric resonance method now promises that gaps in our knowledge of the distribution of electric charge about a molecule will be filled with the help of precision measurements of the electric dipole moment and the moment of inertia. Because this new method can also probe the interactions of the nuclei of atoms with external fields, it would appear that it will become an important tool in further investigations of nuclear and molecular structure.

This problem was proposed to me by Professor I. I. Rabi and executed under his direction. It is a pleasure to thank Professor P. Kusch who gave me considerable help in the last stages of the work and, with Dr. John Trischka, made several runs on the apparatus. I have had many helpful discussions with Professor Willis Lamb on the theory of the experiment, while Professor J. M. B. Kellogg, Dr. S. Millman, and several other members of the Molecular Beam Laboratory have offered suggestions and helped during runs. Mr. S. Cooey of the Physics Department Shop displayed expert workmanship and unusual ingenuity in constructing much of the apparatus.

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

[18] Internationale Tabellen zur Bestimmung von Kristallstrukturen, Vol. II, p. 611.

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

[20] For a discussion of this quantity see W. Gordy, Phys. Rev. **69**, 604 (1946).

[21] Oscar K. Rice, *Electronic Structure and Chemical Binding* (McGraw-Hill Book Company, Inc., New York, 1940), p. 253.

[22] Hannay and Smyth, J. Am. Chem. Soc. **68**, 171 (1946).