FIG. 3. Calibration runs using an annihilation radiation source (Cu^{64}), taken on three consecutive days. (a) Monday, (b) Tuesday, (c) Wednesday. The apparatus was left running continuously over this period.

for our signals of c, within 1%, as measured with a source of annihilation radiation.[5] We were able to obtain a linear delay vs centroid position over a 4×10^{-9}-sec range (Fig. 3), the deviation of any point from the best-fit straight line being less than 3×10^{-11} sec.

DISCUSSION

Table I presents the results of our measurements. In addition to the value of the exponential slopes we also present the centroid shifts of the delayed relative to prompt distribution. (The Au^{198} cascade is not truly prompt and our results are corrected assuming a lifetime of 3×10^{-11} sec for the 411-kev state of Hg^{198}.) The errors presented for the centroid shifts are based on the observed reproducibility of the results. For the reasons mentioned above, we do not consider the centroid shifts to be as systematically reliable as the exponential decay.

TABLE I. Results of the separate lifetime measurements.

Source	Mean life and error (standard deviation) (10^{-10} sec)
	Exponential decay
Hg^{203}	4.06 ± 0.08
Pb^{203}	4.02 ± 0.14
	Centroid displacement
Hg^{203}	4.2 ± 0.1
Pb^{203}	4.3 ± 0.1

Our estimation of systematic errors precludes the combination of the two slope measurement for purposes of reducing the quoted error. We therefore give the final value $(4.05 \pm 0.08) \times 10^{-10}$ sec for the mean life of this state. There is no visible support for the idea that this state is really two closely spaced states.

This measurement is in very good agreement with recent measurements using other techniques.[2] Discussion of this point, as well as the significance of the measured value, is given in this last reference.

During the course of this work another measurement of the lifetime, utilizing equipment similar to ours, was reported by Gorodetsky et al.[7] It is significant that within the small errors quoted our results agree with theirs.[8]

[7] S. Gorodetsky, R. Manquenouille, R. Richert, and A. Knipper, Compt. rend. 251, 65 (1960).

[8] Note added in proof. After submitting this paper a very recent publication by E. C. B. Pederson and R. E. Bell in Nuclear Phys. 21, 393 (1960) has come to our attention. This paper reports a measurement of the Tl^{203*} lifetime using techniques similar to ours. Their result yields $\tau_m = (3.48 \pm 0.15) \times 10^{-10}$ sec which is significantly smaller than our result. We have no explanation for the discrepancy. From the appearance of the data presented, it would seem that the only possible source of this difference can be in the time calibration.

Nuclear Interactions in Deuterium Fluoride*

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The deuteron and fluorine magnetic resonance spectra in the molecule DF have been studied using the molecular beam method. The observed resonance patterns have been compared with those calculated on a UNIVAC computer. The parameters of the calculation were adjusted until the theoretical and the experimental curves matched. In this manner the spin-rotational interaction constant of fluorine in DF was assigned the value $|c_F| = 160 \pm 1$ kc/sec and the quadrupole coupling constant of the deuteron in DF was assigned the value $|d_2| = 34 \pm 4$ kc/sec, which corresponds to $|eqQ/h| = 340 \pm 40$ kc/sec.

I. INTRODUCTION

THE Hamiltonian for a $^1\Sigma$ diatomic molecule in an external magnetic field has been discussed by Ramsey and Lewis.[1] The detailed theory of the molecule

DF in a strong magnetic field is formally identical to that of the molecule HD under the same conditions and that theory has been discussed by Quinn, Baker, LaTourrette, and Ramsey,[2] as well as by Ramsey and Lewis.[1] However, in the case of DF, resolution of the various transitions is not accomplished experimentally. To aid in the interpretation of the composite reso-

[1] N. F. Ramsey and H. R. Lewis, Phys. Rev. 108, 1246 (1957).

[2] W. E. Quinn, J. M. Baker, J. T. LaTourrette, and N. F. Ramsey, Phys. Rev. 112, 1929 (1958).

FIG. 1. Experimental resonance pattern for fluorine transitions in DF. Zero intensity is at 0.5 volt.
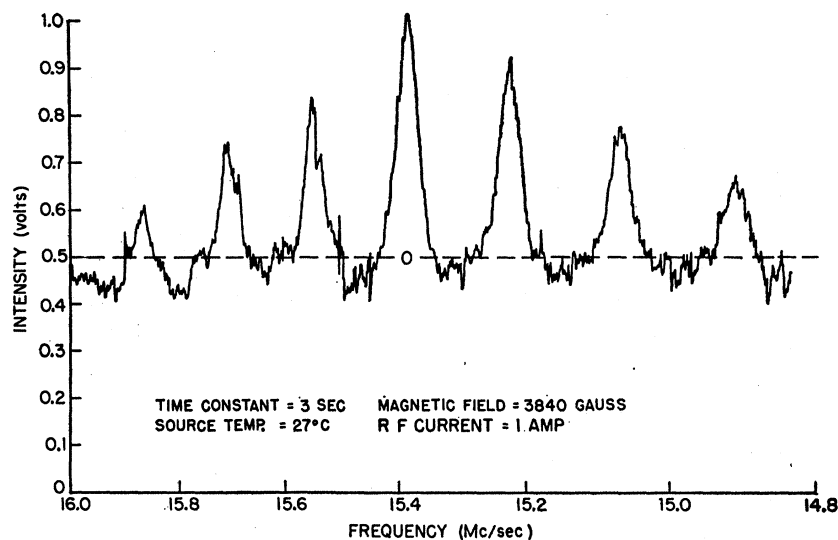
nance patterns obtained for the molecule DF, a calculation has been programmed for the UNIVAC computer[3] which takes account of the probabilities of the various transitions where several resonance lines overlap. This calculation, in effect, predicts by purely mathematical means, the resonance curves to be expected for any arbitrary set of interaction parameters. The various assumed parameters of the Hamiltonian are based either upon experimental results or upon preliminary calculations. The values of these parameters are then adjusted as necessary by successive approximations to give a best match between the theoretical and experimental resonance curves. In the present case, a high-field perturbation calculation was carried out to second order; the parameters which gave the best fit in the second order perturbation calculation, were then finally used in a calculation in which the secular equations for the matrices resulting from the assumed parameters were solved exactly. In this manner, values have been obtained for the spin-rotational interaction constant of fluorine in DF and for the quadrupole coupling constant of the deuteron in DF.

The experiment was performed in the recently completed molecular beam apparatus at Harvard University, a description of which has previously appeared in the literature.[4] For this experiment, the mass spectrometer was set for mass 21, corresponding to DF[+]. The rf region was $\frac{3}{4}$ in. in length. The beam was detected by means of an electron-bombardment ionizer and the resonance was observed with a phase-sensitive detector and on-off modulation of the rf current. The DF used in this experiment was manufactured from AgF_2 and deuterium gas according to the reaction[5]: $AgF_2 + D_2 \rightarrow Ag + 2DF$, the DF being collected in a liquid nitrogen trap.

II. THE FLUORINE INTERACTION

An experimental resonance pattern for the fluorine transitions in DF in a magnetic field of 3840 gauss is shown in Fig. 1. The separated peaks as well as the progressive decline in amplitude for the outlying peaks can be explained on the basis of a large spin-rotational interaction. Although the more precise method of matching calculated and experimental resonance curves was used to obtain the spin-rotational interaction constant, the following qualitative discussion may be helpful in understanding the resonance pattern. Consider the Hamiltonian $\mathcal{3C}$:

$$\frac{\mathcal{3C}}{h} = -\frac{a_D}{|\mathbf{H}|}\mathbf{I}_D \cdot \mathbf{H} - \frac{a_F}{|\mathbf{H}|}\mathbf{I}_F \cdot \mathbf{H} - \frac{b_J}{|\mathbf{H}|}\mathbf{J} \cdot \mathbf{H} - c_F \mathbf{I}_F \cdot \mathbf{J},$$

where the notation of Ramsey and Lewis[1] is employed and where the only non-negligible internal interaction is considered to be the spin-rotational interaction of the fluorine nucleus with the molecular field. For this Hamiltonian, the frequencies corresponding to a reorientation of the fluorine nucleus are given by

$$\nu_F = -a_F - c_F m_J - \frac{c_F^2}{2(a_F - b_J)}[J(J+1) - m_J^2].$$

From this expression, one can see that each of the separated peaks can be interpreted to consist of contributions from several transitions having different J, all of which have the same value of m_J. Furthermore, except for the small third term in the above expression, the peaks should be symmetrically spaced about the fluorine Larmor frequency (for which $m_J = 0$). The variation in height of the side peaks is explained by the fact that the populations of the states for different J are goverened by the expression[6]:

$$N_J \propto (2J+1) \exp[-\hbar^2 J(J+1)/2IkT],$$

[3] N. F. Ramsey (private communication).
[4] M. R. Baker, H. M. Nelson, J. A. Leavitt, and N. F. Ramsey, Phys. Rev. 121, 807 (1961).
[5] J. H. Hildebrand, J. Am. Chem. Soc. 56, 1820 (1934).

[6] G. Herzberg, Spectra of Diatomic Molecules (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1950).
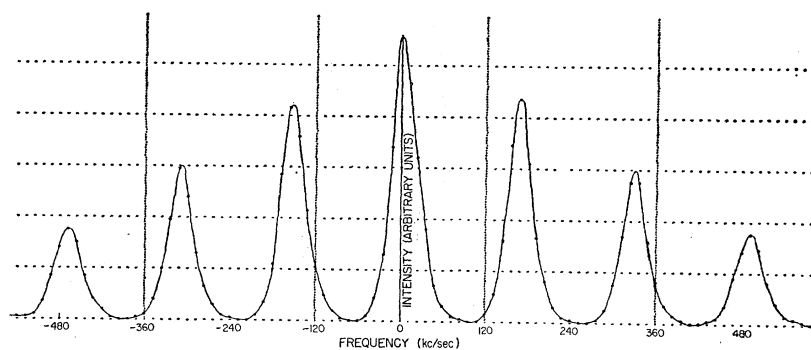
FIG. 2. Theoretical resonance pattern for fluorine transitions in DF. The parameters involved in the calculation were assigned the following values: $a_D = 2.511$ Mc/sec, $a_F = 15.391$ Mc/sec, $b_J = 1.08$ Mc/sec, $c_F = -160$ kc/sec, $c_D = 5.73$ kc/sec, $d_1 = 8.81$ kc/sec, $d_2 = 34$ kc/sec, $\delta = 0.102$ kc/sec. The calculation was carried out for a magnetic field of 3842 gauss and a source temperature of 300°K.

where I is the moment of inertia of the molecule, k is Boltzmann's constant, and T the absolute temperature. The higher J states are, therefore, only sparsely populated for finite temperature and this fact can account for the smaller amplitude of the peaks which correspond to higher m_J.

By subtracting the expression for the frequency of the line corresponding to $+m_J$ from that corresponding to $-m_J$, the following expression results:

$$c_F = \frac{\nu(m_J) - \nu(-m_J)}{2m_J}.$$

From this expression, an approximate value for the spin-rotational interaction constant, c_F, can be obtained by using the frequencies of the maxima of the peaks corresponding to m_J and $-m_J$ in the experimental resonance pattern. From Fig. 1, it is seen that $|c_F|$ is about 160 kc/sec. Figure 1 also shows that the resonance curve should show some asymmetry, but the details of the asymmetry of the resonance pattern are better identified by comparing the experimental curve with the theoretical one obtained by solving the secular equation which is appropriate for the F resonance in DF by means of a UNIVAC computer, as described above. The theoretical curve is shown in Fig. 2. The values of the parameters used in this calculation are as follows:

$a_D = 2.511$ Mc/sec, $a_F = 15.391$ Mc/sec,

$\qquad\qquad\qquad\qquad\qquad b_J = 1.08$ Mc/sec,

$c_F = -160$ kc/sec, $c_D = 5.73$ kc/sec,

$\qquad\qquad\qquad\qquad\qquad d_1 = 8.81$ kc/sec,

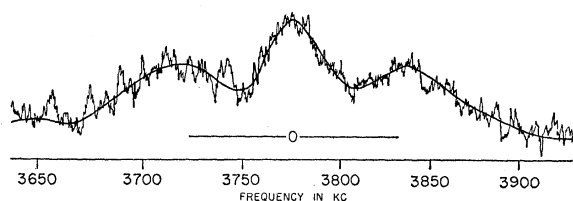$d_2 = 34$ kc/sec, $\delta = 0.102$ kc/sec.

FIG. 3. Experimental resonance pattern for deuteron transitions in DF. Source temperature: 300°K. Magnetic field strength: 5778 gauss. The zero-intensity line is shown.

It can be seen from a study of Figs. 1 and 2, that, with the above values for the parameters of the Hamiltonian, the match between the theoretical curve and the experimental curve is good. This close agreement allows one to assign

$$|c_F| = 160 \pm 1 \text{ kc/sec.}$$

From this experiment, it was not possible to determine the sign of c_F since replacing c_F by $-c_F$ in the UNIVAC calculation made only small changes in the shape of the resonance pattern.

III. THE DEUTERON INTERACTIONS

Figure 3 is an experimental resonance pattern of the deuteron transitions in DF in an external magnetic field of 5778 gauss. The two side peaks are interpreted as arising from the interaction of the electric quadrupole moment of the deuteron with the gradient of the electric field of the molecule at the position of the deuteron. Under the assumption that the side peaks are due to a quadrupole splitting, the separation of these peaks $\Delta\nu$ is approximately related to the quadrupole coupling constant, d_2, by: $d_2 = 4\Delta\nu/15$ for a nucleus with a spin of 1, according to a theory by Feld and Lamb.[7] It is seen from Fig. 3, then, that $d_2 \approx 31$ kc/sec. However, the Feld and Lamb theory neglects interactions other than the quadrupole interaction; it predicts for an infinite temperature a double-peaked pattern which rises vertically up to the maxima from the outside and falling smoothly to a minimum between the peaks. For this special case, Feld and Lamb calculate the separation between maxima to be given by $\Delta\nu = 3eqQ/8h$, or, since $d_2 = eqQ/10h$, $\Delta\nu = 15\ d_2/4$, as stated above. For the present experiment, however, the quadrupole interaction is not the sole significant one, and the effect of the other interactions is to smear out the sharply rising peaks of the Feld and Lamb theory and to bring the maxima of the peaks closer together so that $\Delta\nu$ is slightly less than $15\ d_2/4$.

Again, the value assigned to the parameter d_2 (or eqQ) was determined by comparison of the experimental and calculated resonance patterns. Figure 4 is the curve which was obtained from the UNIVAC solution of the secular equation appropriate for the deuteron resonance

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

FIG. 4. Theoretical resonance pattern for deuteron transitions in DF. The parameters of the calculation were assigned the following values: $a_D = 2.511$ Mc/sec, $a_F = 15.391$ Mc/sec, $b_J = 1.08$ Mc/sec, $c_F = -160$ kc/sec, $c_D = 5.73$ kc/sec, $d_1 = 8.81$ kc/sec, $d_2 = 34$ kc/sec, $\delta = 0.102$ kc/sec. The calculation was carried out for a magnetic field of 5778 gauss and a source temperature of 300°K. The dashed curve is the result of solving the secular equation. The solid curve shows the result of multiplying the contribution of the $J = 0$ states by a factor of three.
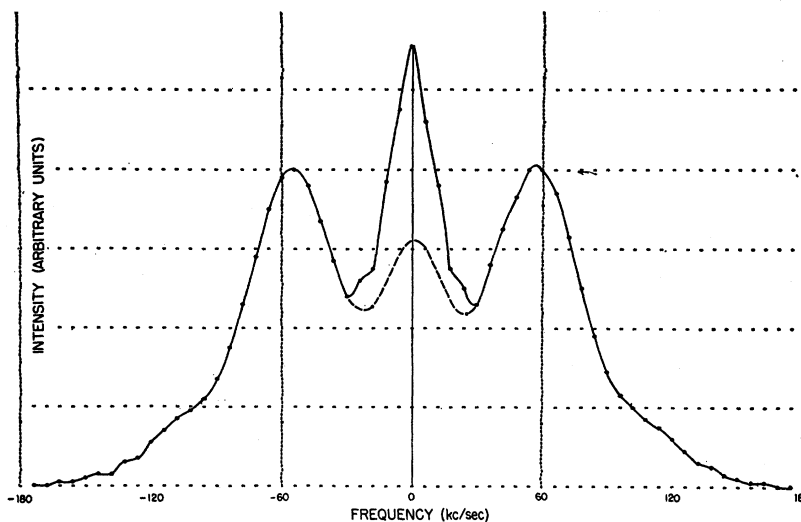
in DF in a magnetic field of 5778 gauss. The values assigned to the parameters of the calculation are the same as those given above for the theoretical fluorine resonance pattern. In particular, d_2 is given the value of 34 kc/sec.

The theory of Feld and Lamb for the shape of the resonance pattern when a quadrupole interaction exists, applies to the case of infinite temperature so that a vanishing fraction of the molecules remain in the $J = 0$ state. This theory predicts no central peak for the deuteron resonance in DF, in contrast with the experimental results. However, for a finite temperature, a non-negligible fraction of the molecules exist in the $J = 0$ state and these molecules give rise to the central peak of the resonance pattern. Actually, any state that is little affected by the quadrupole interaction will contribute to the central peak. Examples of such states are those for which the expression $3m_J^2 - J(J+1)$ vanishes or is very small since this expression occurs as a factor in the quadrupole interaction term of the Hamiltonian. The first version of the theoretical resonance curve had a central peak which was smaller than the side peaks as is shown by the dashed curve in Fig. 4. It was suggested by James Pinkerton that a large central peak might be explained upon the basis of multiple quantum transitions, i.e., transitions for which $\Delta m_D > 1$. Such transitions would effectively increase the throw-out power for the particular molecules involved and would increase the apparent amplitude of the resonance peak at the frequencies where such multiple transitions occur. The solid curve of Fig. 4 shows the effect upon the theoretical resonance pattern of multiplying the contribution of the $J = 0$ states to the reso-

nance curve by a factor of three, indicating in a qualitative way that multiple quantum transitions might account for the shape of the deuteron resonance curve in DF.

IV. CONCLUSIONS

Because of the excellent agreement between the experimental and the theoretical resonance curves for the fluorine transitions in DF, it is concluded that the fluorine spin-rotational interaction constant in the molecule has the value: $|c_F| = 160 \pm 1$ kc/sec. A discussion of the large spin-rotational interaction exhibited by fluorine is found in a previous paper.[4] It is interesting to note here, however, that the spin-rotational interaction constant of fluorine in DF calculated on the basis of a bare-nucleus model[8] is $c_F = +29$ kc/sec, indicating that the constant is actually predominantly due to the motion of the electrons of the rotating molecule. From the above value of c_F, one would predict, on the basis of the change in moment of inertia, that the spin-rotational interaction constant for fluorine in HF would be 304 kc/sec. This result is in agreement with experiment.[4]

The deuteron resonance pattern in DF can be explained by assigning the following value to the quadrupole coupling constant:

$$|d_2| = 34 \pm 4 \text{ kc/sec,}$$

so that $|eqQ/h| = 340 \pm 40$ kc/sec. In addition it would seem that multiple quantum transitions occur which emphasize the central peak of the experimental resonance.

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