P. Favero and J. G. Baker
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Anomalous Stark Effects in the Millimetre Wave Spectrum of Formyl Fluoride (*).

P. Favero (**) (*,*) and J. G. Baker

Department of Physics, Duke University - Durham, North Carolina

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Summary. — Measurements of Stark effects in the rotational spectra of formyl and *d*-formyl fluoride show the presence of anomalous components that vary in strength with the field. They occur predominantly at high fields and may possibly be a molecular polarisability effect. In addition the normal molecular dipole moment is found to be (1.99 ± 0.03) *D*, oriented almost parallel to the C-H bond and at an angle of 79° to the C-F bond. This is discussed in connection with the molecular structure.

1. – Introduction.

In a previous investigation of the rotational spectrum of formyl fluoride (¹) a curious doubling of some Stark components was noted. The present work studies this phenomenon in more detail and also yields a value for the molecular dipole moment from measurements of the shift of the Stark components at various fields. Measurements of this kind in the millimetre wave region have been restricted to light molecules (²,³,⁴) because Stark effects tend to fall off rapidly with increasing J; however in the case of asymmetric top mole-

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(**) Present address: Istituto di Chimica Fisica, Università di Padova, Italy.

(*,*) International Fellow of the National Academy of Sciences through International Cooperation Administration.

(¹) P. Favero, A. M. Mirri and J. G. Baker: *Journ. Chem. Phys.*, **31**, 556 (1959).

(²) R. Trambarulo, S. N. Ghosh, C. A. Burrus and W. Gordy: *Journ. Chem. Phys.*, **21**, 851 (1953).

(³) C. A. Burrus: *Journ. Chem. Phys.*, **28**, 427 (1958).

(⁴) B. Bhattacharya and W. Gordy: *Phys. Rev.*, in press; also D. M. Larkin: private communication.

cules the decrease is relatively slow and is counterbalanced by the higher fields that may be obtained by using a smaller Stark cell.

2. – Experimental.

The spectrometer and 1 meter *K* band Stark cell used have been described elsewhere (2,5). Observations were made with a 4 000 Hz zero-based square wave voltage variable from 0 to 1 000 V and measured by a peak to peak voltmeter. Lines and Stark components were detected by a lock-in amplifier and recorder or persistent screen oscilloscope (the latter by sweeping the klystron reflector with a 0.1 Hz saw-tooth wave form). The cell was calibrated by observations on the 0 → 1 transition of HCN at 88 632 MHz, for which very accurate measurements are available (4). The strongest components were followed up to fields of 4 000 V/cm and frequency shifts of 130 MHz before they were appreciably broadened by field inhomogeneities. However, the limiting accuracy was found to lie in reading the scale of the peak to peak voltmeter, which could not be done to better than 1 %.

3. – Discussion.

The recorder tracings of Fig. 1 are typical of the patterns observed. It will be noted that doubling usually appears at fields of (1500÷2000) V/cm and the doublet splitting steadily increases with field. At the same time one component of the doublet remains constant in strength while the other increases rapidly. Frequency measurements have been made on all resolved Stark components of four transitions of HCOF

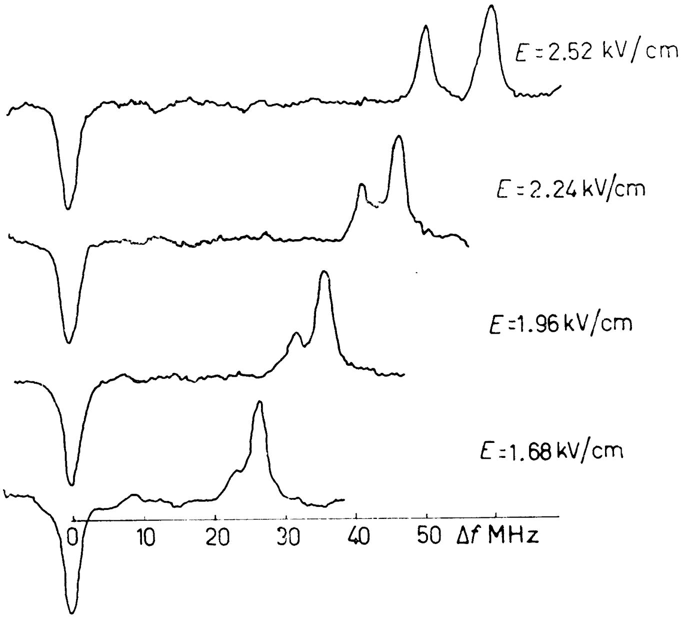

Fig. 1. – The $0_{00} \rightarrow 1_{11}$ transition of HCOF at 101 550.36 MHz. Stark components at various field strengths.

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(5) P. Favero, A. M. Mirri and J. G. Baker: *Nuovo Cimento*, to be published.

and one transition of DCOF at fields ranging from 1 000 to 4 000 V/cm. The results are summarized in Table I which gives values of $\Delta f/E^2$ averaged over

TABLE I. – *Stark effect measurements.*

Transition	M value	$\Delta f/E^2$ MHz (kV/cm)^2 Observed	Calculated
$0_{00}\to 1_{11}$	0	9.4	9.37
	0''	8.3	
$1_{01}\to 2_{12}$	0	10.6 (broad)	9.30
	1	(unresolved)	11.03
$5_{05}\to 5_{14}$	3	1.00	1.02
	3''	1.23	
	4	3.8_9	3.79
	4''	4.6_5	
	5	7.4_5	7.34
	5''	8.5	
$6_{06}\to 6_{15}$	5	4.2_5	4.21
	6	6.7	6.79
	6''	7.9_5	
$1_{01}\to 2_{12}$ (DCOF)	0	-3.9_5	-3.98
	1	$+0.83$	$+0.81$
	1''	perceptible resolution at 4 000 V/cm.	

Double primes denote anomalous components.

several measurements, with deviations up to 2 % as expected from the voltmeter reading error. The normal components move linearly with E^2 as expected for an asymmetric top; the anomalous components (that is those varying in strength with field) do the same but with a markedly different slope. They also show some tendency to project back to a point that is not the unsplit line frequency, but experimental error is too large to give this tendency real significance. Fig. 2 shows a plot of the two components of the $0_{00}\to 1_{11}$ transition. These two are especially significant because this transition should have only one component ($M=0$) and no perturbation would be expected to split this, as might happen for components of higher M.

Considerable care was taken to eliminate the possibility that this phenomenon was caused by an equipment defect. A two-valued field caused by incorrect alignment of the Stark electrode does not account for the field dependence or the irregular slope of the anomalous components; furthermore no such effect was observed in the case of HCN although experimental conditions were the same. Irregularities in the square wave used would also have been noted for HCN. The field modulation was eliminated as a cause by carrying out video observations with a DC voltage taken from the rectifiers of the square wave generator; although the Stark components of the Table I transitions were a little too weak to measure, the doubling and intensity changes were clearly visible.

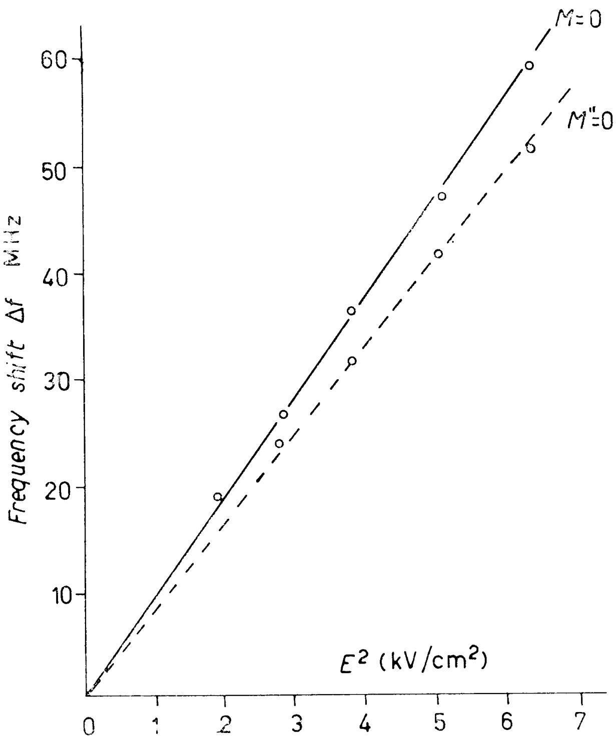

Fig. 2. – Stark displacements of $M = 0$, $M'' = 0$ components of the $0_{00} \to 1_{11}$ transition.

Calculations show that the anomalous components are not transitions of the form $\Delta M = \pm 1$, normally forbidden in the type of cell used here. A number of other cases of forbidden transitions produced by an electric field have been discussed (6) but none seem to correspond closely to the present work. The effect seems to be one of such high molecular polarizability that an electric field can appreciably change the dipole moment. It is interesting to speculate on the uniqueness of this effect, for, although it has never been reported previously, work at fields of (2 000 ÷ 4 000) V/cm has as yet been restricted to linear molecules. There is a considerable difference even between the two formyl fluoride isotopes, for in the DCOF transition of Table I the doubling only begins to appear at 4 000 V/cm. DC field observations on the $8_{08} \to 8_{17}$ and $9_{09} \to 9_{18}$ transitions of this molecule similarly showed a doubling that just appeared at the highest available fields.

It seems that more accurate measurements at high fields on several molecules will be needed before this phenomenon of field dependent Stark doubling can be satisfactorily accounted for.

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(6) C. H. Townes and A. L. Schawlow: *Microwave Spectroscopy* (New York, 1955), chap. 10.

4. – Dipole moment measurement.

Measurements on the normal Stark components have been fitted to the equation of Golden and Wilson (⁷):

$$\Delta W = (A + BM^2)E^2 ,$$

where A and B are complicated functions of the molecular transition probabilities and rotational energy differences. Although tables of the former are available (⁸) they are very widely spaced and it was found more satisfactory to calculate the required values from symmetric top transition probabilities and the asymmetric top transformation appropriate to the observed rotational constants (⁵). The dipole moment components of Table II fit the Table I measurements to approximately 2 %. It is interesting that μ_b for DCOF is significantly larger than for HCOF. This effect appears in addition to the change due to a slight rotation of the principal axes of inertia. Although previous work (⁵) shows this rotation to be very slight (~ 1°) it does account for part of the change in the dipole moment components in going from HCOF to DCOF. Very accurate measurements would give a method of locating the position of the H atom, in the molecule, at present rather uncertain due to zero-point vibrations, by means of this rotation.

TABLE II. – *Dipole moment components.*

	HCOF	DCOF
μ_a	$(0.58 \pm 0.02)\ D$	$(0.61 \pm 0.02)\ D$
μ_b	$(1.91 \pm 0.03)\ D$	$(1.96 \pm 0.03)\ D$

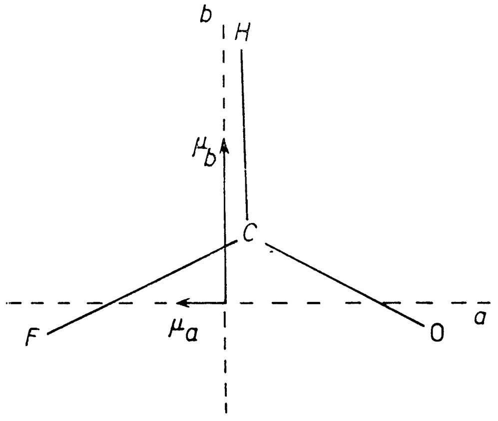

Fig. 3. – Principal inertial axes of HCOF.

This isotopic shift in μ_a allows determination of its orientation. Examination of the molecular centre-of-gravity co-ordinates shows that the principal axes are located as in Fig. 3.

The change to DCOF will result in a rotation of the b axis towards the D atom. There is little doubt that μ_b is oriented with the H atom positive

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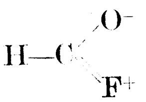
(⁷) S. GOLDEN and E. B. WILSON: *Journ. Chem. Phys.*, **16**, 669 (1948).

(⁸) P. C. CROSS, R. M. HAINER and G. W. KING: *Journ. Chem. Phys.*, **12**, 210 (1944).

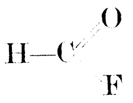
and the O and F atoms negative, and so for μ_a to increase on D substitution its orientation must be as shown. The total dipole moment of the molecule therefore has the value 1.99 ± 0.03 D and is oriented at 79° to the C–F bond and 13° to the C–H bond, with the hydrogen atom end positive.

Previously (⁵) three resonating structures were postulated on the basis of the observed bond lengths.

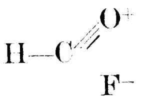
I



II



III



It now appears that the dipole moment corresponds more closely to structure I than to III, despite the bond lengths correspond better to III.

5. – Conclusion.

The existence of an anomalous doubling of the Stark components of formy fluoride has been confirmed but there is no very satisfactory explanation for this. The normal molecular dipole moment is in excellent agreement with that determined by **Leblanc**, **Laurie** and **Gwinn** (⁹) both in direction and orientation. These workers do not report any Stark doubling, but it would appear that they may not have reached sufficiently high fields with the Stark cell they described unless their square wave voltage was considerably higher than ours. Certainly much work remains to be done on this topic before it can be satisfactorily understood.

(⁹) D. Leblanc, V. W. Laurie and W. D. Gwinn: to be published.

Note added in proof.

D. M. Larkin of the Physics Dept., Duke University, has examined the reported lines of HCOF further in a parallel plate Stark cell (⁴) and finds no doubling at fields up to 5 000 V/cm. We feel that the arguments presented in the text are still valid, and it appears that if the extra Stark components are indeed spurious a new kind of equipment defect that merits much further investigation is occurring.

RIASSUNTO

La misura dell'effetto Stark nello spettro rotazionale del fluoruro di formile ha mostrato la presenza di componenti anomale che cambiano di intensità con il campo. Esse si presentano a campi elevati e possono essere dovute ad un effetto di polarizzazione molecolare. È stato determinato il momento dipolare normale il cui valore è (1.99 ± 0.03) D; esso è orientato quasi parallelamente al legame C–H e fa un angolo di 79° con il legame C–F. Questi dati sperimentali vengono discussi in connessione con la struttura molecolare.