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Microwave Spectra, Dipole Moments, and Torsional Potential Constants of *cis*- and *trans*-Cyclopropanecarboxylic Acid Fluoride*

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Microwave spectra have been assigned for the ground state and several excited torsional states of species of cyclopropanecarboxylic acid fluoride with the oxygen atom *cis* and *trans* to the cyclopropane ring. Dipole moments obtained by analysis of the Stark effect are as follows: *trans* species: $\mu_a=3.43\pm0.03$ D, $\mu_b=0.44\pm0.05$ D, $\mu_c=0$, $\mu=3.46\pm0.03$ D; *cis* species: $\mu_a=2.85\pm0.03$ D, $\mu_b=1.63\pm0.03$ D, $\mu_c=0$, $\mu=3.28\pm0.03$ D. By analysis of estimates of the torsional excitation energies of the two species and the *cis–trans* energy difference, values of the first three coefficients of a Fourier expansion of the torsional potential have been obtained as follows: $V_1=-1520\pm320$ cal/mole, $V_2=5150\pm700$ cal/mole, $V_3=990\pm260$ cal/mole.

I. INTRODUCTION

In the preceding paper[1] the first three coefficients of a Fourier expansion of the torsional potential were estimated for cyclopropanecarboxaldehyde. The torsional potential was found to be dominated by a large V_2 coefficient ($V_2=4.39$ kcal/mole) confirming the results of a previous electron diffraction investigation[2] which showed that the molecule occurred as conformers with the oxygen atom *cis* and *trans* to the cyclopropane ring. The value of V_3 in cyclopropanecarboxaldehyde (0.27 kcal/mole) was found to be considerably less than V_3 for acetaldehyde (1.17 kcal/mole).[3] In order to compare these numbers with values for a compound with a similar structure, a sample of cyclopropanecarboxylic acid fluoride was prepared and its microwave spectrum analyzed. The acid fluoride was selected for study because the substitution of fluorine for hydrogen in the aldehyde group introduces an atom with p lone-pair electrons which can contribute charge to the basic π-electron system of the CO bond. If the large V_2 in the aldehyde is a result of conjugation of the ring with the CO bond, the extra π-electron density in the acid fluoride should increase the conjugation and therefore increase V_2.

II. EXPERIMENTAL

The sample of cyclopropanecarboxylic acid fluoride was prepared by passing cyclopropanecarboxylic acid chloride back and forth over antimony trifluoride in a vacuum system until the infrared spectrum showed the acid chloride concentration to be less than about 5%. Because of the lower vapor pressure and weaker spectrum, there was no interference from the acid chloride at this concentration. The acid fluoride had to be stored at dry-ice temperature to inhibit decomposition.

The spectrum was examined with conventional 90 and 100-kHz Stark-modulated spectrometers employing klystron and backward-wave oscillator radiation sources The methods for measuring Stark effects and relative intensities of spectral lines are described in I.

III. MICROWAVE SPECTRUM

By analogy with cyclopropanecarboxaldehyde, species of cyclopropanecarboxylic acid fluoride with the oxygen atom *trans* and *cis* to the cyclopropane ring were expected. Projections of the *cis* and *trans* species based on assumed structures are shown in Fig. 1. Preliminary calculations indicated that a and b-type transitions should occur for both species. The a-type $J=1$–2 transitions for both rotamers were identified first by their characteristic Stark effect. The transitions for the *cis* conformer were considerably more intense, and b-type Q-branch lines were assigned for this species. However, only a-type transitions could be identified for the *trans* species.

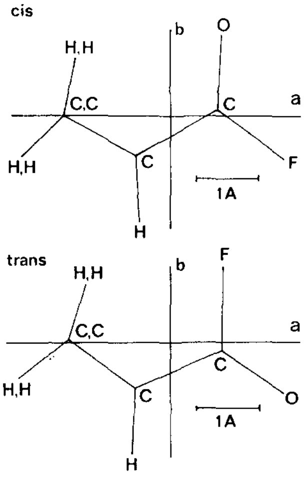

FIG. 1. Projections of *cis*- and *trans*-cyclopropanecarboxylic acid fluoride in their respective planes of symmetry.

Some difficulty was encountered at first in trying to locate transitions in excited torsional states of the *trans* species. This turned out to be due to the fact that the excited state lines lie close to the ground-state transitions, the separation being only 1 or 2 MHz in some cases. Ultimately, however, transitions for the ground and two excited torsional states of the *trans* rotamer were identified and the frequencies of these transitions are given in Table I.

Excited-state transitions could be assigned without difficulty for the *cis* conformer. Transitions up to and including the sixth excited state were seen, but enough frequencies for an assignment were obtained only through $v=4$. The measured frequencies for the *cis*

TABLE I. Observed[a] and observed minus calculated (in parentheses) frequencies[b] for *trans*-cyclopropanecarboxylic acid fluoride.

Transition	$v=0$	$v=1$	$v=2$
$1_{11}-2_{12}$	10 105.55(0.04)	10 109.72(0.05)	10 113.03(−0.05)
$1_{10}-2_{11}$	10 887.86(−0.03)		
$1_{01}-2_{02}$	10 472.68(0.08)		
$2_{02}-3_{03}$	15 649.25(0.02)	15 652.48(−0.04)	15 654.68(0.00)
$2_{12}-3_{13}$	15 143.64(0.01)	15 150.08(0.08)	15 155.20(0.06)
$3_{03}-4_{04}$	20 757.68(0.00)	20 763.03(0.03)	
$3_{13}-4_{14}$	20 165.34(−0.06)	20 174.11(−0.09)	20 181.08(−0.02)
$3_{22}-4_{23}$	20 974.61(−0.02)		
$6_{06}-7_{07}$	35 612.02(−0.54)		
$6_{25}-7_{26}$	36 551.54(−0.65)		

[a] Observed frequencies are ±0.05 MHz.

[b] In megahertz.

conformer for the ground and four excited states of the torsion are shown in Table II.

Rotational constants for the *trans* species are given in Table III and for the *cis* species in Table IV. Derived values of the moments of inertia (I_α, $\alpha=a, b, c$) and the second moments [$P_{\alpha\alpha}=\frac{1}{2}(I_\beta+I_\gamma-I_\alpha)$] are also shown in Tables III and IV. The A rotational constants were not accurately obtained for the *trans* species because of the low A dependence of the transitions observed. Furthermore, there is some evidence from the Stark effect (discussed below) that the A value in Table III, which was obtained from a fit of the observed frequencies, is too large. Consequently, I_a and the second moments in Table III have higher uncertainties than the other entries in both tables. Nevertheless, since P_{cc} is very sensitive to out-of-plane rotation of the aldehyde group (P_{cc} is calculated to be 17.4 uA^2 for 30° rotation out of plane for the *trans* species), the accuracy of P_{cc} is sufficient in both Tables III and IV to provide strong evidence that the two species each have a plane of symmetry.[4]

IV. STARK EFFECT

Comparisons of observed and calculated Stark shifts for the *trans* and *cis* species are shown in Tables V and VI, respectively. The observed Stark shifts for both species were first fit by least squares assuming nonzero values for all three dipole-moment components. For the *cis* species the value obtained for μ_c^2 was -0.065 D^2, which is zero within the experimental uncertainty. Hence, μ_c was set equal to zero in a second calculation, and the results of this calculation appear in Table VI. For the *cis* species $\mu_a=2.85\pm0.03$ D, $\mu_b=1.63\pm0.03$ D, and $\mu=3.28\pm0.03$ D.

For the *trans* species two problems arose in the fitting of the experimental Stark shift slopes. First, one of the calculated slopes—for the $M=0$ component of the $2_{12}-2_{13}$ transition—deviated from the experimental

TABLE II. Observed[a] and observed minus calculated (in parentheses) frequencies[b] for *cis*-cyclopropanecarboxylic acid fluoride.

Transition	$v=0$	$v=1$	$v=2$	$v=3$	$v=4$
$1_{01}-2_{02}$	10 010.07(0.01)	10 022.23(0.02)	10 033.88(0.00)	10 045.01(0.00)	
$1_{10}-2_{11}$	10 367.79(−0.01)				
$1_{01}-2_{12}$	14 549.61(0.00)				
$2_{02}-3_{03}$	14 972.28(0.04)				15 041.00(0.00)
$2_{12}-3_{13}$	14 519.91(0.17)				
$3_{12}-3_{21}$	14 174.70(0.05)				
$4_{13}-4_{22}$	13 686.46(0.01)				
$2_{11}-3_{12}$	15 540.55(−0.07)				
$5_{14}-6_{23}$	13 210.74(−0.01)				
$6_{06}-6_{15}$	9 474.12(−0.49)	9 416.13(−0.06)	9 359.37(0.03)	9 303.71(−0.05)	
$6_{15}-6_{24}$	12 825.65(0.00)	12 743.77(−0.26)	12 666.05(−0.33)	12 592.38(−0.24)	12 522.24(−0.03)
$7_{07}-7_{16}$	11 252.22(−0.78)	11 183.81(−0.18)	11 116.58(0.02)	11 050.16(−0.18)	
$7_{16}-7_{25}$	12 608.88(0.05)	12 528.67(−0.10)	12 452.31(−0.18)	12 379.72(−0.14)	12 310.64(0.05)
$8_{08}-8_{17}$	13 380.87(−1.24)	13 300.40(0.02)	13 220.09(−0.20)		
$8_{17}-8_{26}$	12 630.18(0.15)	12 550.28(0.10)	12 473.99(0.13)	12 401.02(0.10)	12 331.28(−0.02)
$9_{18}-9_{27}$	12 947.81(0.24)	12 866.63(0.42)	12 788.63(0.53)	12 713.57(0.53)	
$10_{19}-10_{28}$	13 609.47(0.54)				

[a] Observed frequencies are ±0.05 MHz.

[b] In megahertz.

TABLE III. Rotational constants,[a] moments of inertia,[b] and second moments[c] for *trans*-cyclopropanecarboxylic acid fluoride.

	$v=0$	$v=1$	$v=2$
A	7380	7361	7318
B	2819.77	2818.90	2818.20
C	2428.58	2430.25	2431.62
I_a	68.479	68.656	69.059
I_b	179.2260	179.2813	179.3258
I_c	208.0953	207.9523	207.8351
P_{aa}	159.421	159.289	159.051
P_{bb}	48.674	48.664	48.784
P_{cc}	19.805	19.992	20.274

[a] In megahertz. Uncertainties in rotational constants are as follows: A, ±20 MHz; B, ±0.05 MHz; C, ±0.05 MHz.

[b] In unified mass units·angstroms squared. Conversion factor: 505 376 MHz·uÅ².

[c] In unified mass units·angstroms squared.

TABLE V. Stark effect and dipole moment of *trans*-cyclopropanecarboxylic acid fluoride.

Transition	$(\partial\nu/\partial E^2)_{\text{obs}}$[a,b]	$(\partial\nu/\partial E^2)_{\text{calc}}$[a]
1_{01}–2_{02} $M=1$	73.00	72.61
1_{10}–2_{11} $M=0$	67.16	67.95
1_{11}–2_{12} $M=0$	72.13	72.39
4_{23}–5_{25} $M=0$	0.399	0.441
	$\mu_a=3.43\pm0.03$ D	
	$\mu_b=0.44\pm0.05$ D	
	$\mu_c=0.0$	
	$\mu=3.46\pm0.03$ D	

[a] Hz (V/cm)$^{-2}$. $\mu_{\text{OCS}}=0.7152$ D assumed.

[b] Uncertainty in observed slopes is ±1.5%.

value by approximately 20%. Second, there was a strong linear dependence between μ_b^2 and μ_c^2. A survey of the Stark coefficients of all the low J transitions in the available microwave region failed to uncover any transition which had both a μ_c^2 coefficient of reasonable size and a significantly different μ_b^2 coefficient. As a result, the linear dependence between μ_b^2 and μ_c^2 could not be broken, and final fitting had to be done assuming a plane of symmetry (i.e., assuming $\mu_c^2=0$).

The Stark effect of the $M=0$ component of the 2_{12}–3_{13} transition was reinvestigated including data at higher Stark fields. It was found that the Stark shifts showed significant deviation from a straight line when plotted against the square of the electric field. This behavior was traced to a near degeneracy of the 2_{20} and the 3_{13} energy levels. Calculations, based on direct diagonalization of the Hamiltonian matrix including the Stark effect for all levels up to and including $J=5$, showed that the calculated Stark shift of the 3_{13} level is strongly dependent on the values assumed for μ_b^2 and for the A rotational constant. Exhaustive calculations were not carried out owing to the difficulty of properly weighting these factors together with the Stark shifts of the other transitions studied. However, calculations assuming μ_a^2 and μ_b^2 near the values in Table VI showed that the A rotational constant must be 20–40 MHz smaller than the value shown in Table III.

The results of the final least-squares fit of Stark shift slopes for the *trans* species is shown in Table V. The dipole moments are $\mu_a=3.43\pm0.03$ D, $\mu_b=0.44\pm0.05$ D, and $\mu=3.46\pm0.03$ D.

The values of the components of the dipole moment were useful in helping to sort out which spectrum belonged to which species. The initial assignment was based on a comparison of the moments of inertia derived from the observed rotational constants with those calculated from assumed structures. Unfortunately, the oxygen- and fluorine-atom masses do not differ greatly, and as may be seen from Tables III and IV the moments of inertia of the two species are not very different. However, the orientation of the dipole moment with respect to the principal axes is very different in the two species. Using bond moments for CO derived from the dipole moment of acetaldehyde (2.7 D)[3] and for CF derived from ethyl fluoride (1.9 D),[5] the ratio of μ_a to μ_b can be calculated for both species and compared to the experimental ratios. The calculated ratios are 5.42

TABLE IV. Rotational constants,[a] moments of inertia,[b] and second moments[c] for *cis*-cyclopropanecarboxylic acid fluoride.

	$v=0$	$v=1$	$v=2$	$v=3$	$v=4$
A	7539.83	7510.94	7483.40	7457.12	7431.97
B	2677.07	2679.06	2680.93	2682.66	2684.23
C	2336.59	2340.63	2344.54	2348.29	2351.81
I_a	67.0275	67.2853	67.5329	67.7709	68.0003
I_b	188.7795	188.6393	188.5077	188.3862	188.2760
I_c	216.2878	215.9145	215.5544	215.2102	214.8881
P_{aa}	169.0199	168.6342	168.2646	167.9127	167.5819
P_{bb}	47.2679	47.2802	47.2898	47.2974	47.3062
P_{cc}	19.7596	20.0050	20.2431	20.4734	20.6941

[a] Uncertainties in the rotational constants are as follows: A, ±0.05 MHz; B, ±0.05 MHz; C, ±0.05 MHz.

[b] In unified mass units·angstroms squared. Conversion factor: 505 376 MHz·uÅ².

[c] In unified mass units·angstroms squared.

and 1.23 for the *trans* and *cis* species, respectively, whereas the corresponding observed ratios are 7.80 and 1.75, providing strong evidence that the assignment is correct.

V. RELATIVE INTENSITIES AND TORSIONAL POTENTIAL

The small frequency separation between ground- and excited-state lines together with the high density of lines severely limited the number of transitions favorable for intensity measurements in the *trans* species. Only two low-frequency lines, the 1_{11}–2_{12} near 10 100 MHz and 2_{12}–3_{13} near 15 150 MHz were deemed suitable for study. Also, in both of these cases only the ground- to first excited-state intensity ratio was measured. The measured intensity ratios (r) were converted to energies by means of the relation E (cm^{-1}) $= 0.695T\ln(r)$. Twenty-six measurements for 1_{11}–2_{12} transitions gave an average value of 89.8 cm^{-1} for the torsional excitation, and six measurements on the 2_{12}–3_{13} transition gave a value of 91.3 cm^{-1}. These numbers are summarized in Table VII. As indicated in I these measurements were all made under different microwave conditions and sample pressures. A rounded value of 90±5 cm^{-1} is selected for the torsional excitation energy of the *trans* species.

TABLE VI. Stark effect and dipole moment of *cis*-cyclopropanecarboxylic acid fluoride.

Transition	$(\partial\nu/\partial E^2)_{\text{obs}}$[a,b]	$(\partial\nu/\partial E^2)_{\text{calc}}$[a]
1_{01}–2_{02} $M=0$	−49.47	−49.13
1_{01}–2_{02} $M=1$	81.36	81.27
1_{10}–2_{11} $M=0$	51.47	50.66
2_{02}–3_{03} $M=0$	−12.23	−12.20
2_{02}–3_{03} $M=2$	44.77	45.11
2_{12}–3_{13} $M=1$	43.19	44.40
	$\mu_a=2.85\pm0.03$ D	
	$\mu_b=1.63\pm0.03$ D	
	$\mu_c=0.0$	
	$\mu=3.28\pm0.03$ D	

[a] Hz (V/cm)$^{-2}$. $\mu_{\text{OCS}}=0.7152$ D assumed.

[b] Uncertainty in observed slopes is ±1.5%.

A large number of transitions could be used for intensity measurements in the *cis* species. These are summarized in Table VIII. For each of these transitions relative intensities of the ground- and first two excited-state lines were measured. The intensity ratios $(v=1)/(v=0)$, $(v=2)/(v=1)$, and $(v=3)/(v=1)$ were converted to energy differences E_{01}, E_{12}, and E_{13} and the values of E_{01}, E_{12}, and $\frac{1}{2}E_{13}$ were averaged to yield the excitation energy shown in Table VIII. Because data from more than one excited state were used, the correction described in I was applied to yield a value of 63.3±4 cm^{-1} for the excitation energy of the *cis* species.

For the *cis*–*trans* energy separation 18 values were obtained for the ratio of the intensities of the *cis* 1_{01}–2_{02} transition (10 010.07 MHz) to that of the *trans* 1_{11}–2_{12} transition (10 105.55 MHz). The rounded average energy difference derived from these ratios is 200±30 cm^{-1} with the *trans* species having the higher energy.

TABLE VII. Energy separation[a] between the ground and first excited torsional states for *trans*-cyclopropanecarboxylic acid fluoride.

Transition	Number of averages	Energy
1_{11}–2_{12}	26	89.8
2_{12}–3_{13}	6	91.3
	Weighted average	90.1

[a] In cm^{-1}.

The first three Fourier coefficients of the torsional potential,

$$V=\sum_n \tfrac{1}{2}V_n(1-\cos n\theta),$$

assuming $\theta=0$ in the *trans* configuration, were obtained from the excitation energies of the two species and the *cis*–*trans* energy difference assuming $V_n=0$ for $n\geq4$. As described in detail in I, a harmonic approximation was employed at first to obtain approximate values of the V_n, and these values were later refined by comparison of the experimental energies with the appropriate energy eigenvalues of the Hamiltonian,

$$H=F_0p^2+F_1p\cos\theta p+\sum_{n=1}^{3}\tfrac{1}{2}V_n(1-\cos n\theta).$$

Values of the kinetic-energy coefficients F_0 and F_1 were obtained by means of Knopp and Quade's[6] equations as follows:

$$F_0=0.8641\text{ cm}^{-1},\qquad F_1=0.0107\text{ cm}^{-1}.$$

TABLE VIII. Energy separation[a] between successive torsional states for *cis*-cyclopropanecarboxylic acid fluoride.

Transition	Number of averages	Energy
1_{11}–2_{12}	18	61.10
1_{01}–2_{02}	17	63.21
2_{02}–3_{03}	3	66.21
6_{06}–6_{15}	2	74.07
7_{07}–7_{16}	10	69.33
7_{16}–7_{25}	6	60.66
8_{17}–8_{26}	6	60.66
10_{19}–10_{28}	3	65.36
11_{110}–11_{29}	3	64.50
	Weighted average	63.71

[a] In cm^{-1}.

TABLE IX. Torsional excitation energies, *cis–trans* energy difference, and torsional potential constants[a] for cyclopropanecarboxylic acid fluoride.

Parameter	(cm^{-1})	(cal/mole)
Excitation energy, *trans*	90±5	257±14
Excitation energy, *cis*	63.3±4	181±11
$E_0(cis)-E_0(trans)$	−200±30	−572±85
V_1	−530±110[b]	−1520±320
V_2	1800±240	5150±700
V_3	345±90	990±260

[a] The potential constants are defined such that the torsional angle is zero in the configuration in which the oxygen atom is *trans* to the ring.

[b] The uncertainties in the potential constants are propagated experimental uncertainties plus 5%, the estimated uncertainty in the values assumed for the reduced moments of inertia. A three-term potential function is assumed; the additional uncertainty due to neglect of V_4 and V_5 are $\delta V_1=2V_5$, $\delta V_2=-4V_4$, $\delta V_3=-3V_5$.

The final values of the potential constants are $V_1=-530\pm110$ cm^{-1}, $V_2=1800\pm240$ cm^{-1}, and $V_3=345\pm90$ cm^{-1}. The values of the various energy differences and the V_n are summarized in Table IX.

The maximum value of the torsional potential described by the constants just given occurs at $\theta=78.7°$ and is 5.17±0.71 kcal/mole. This value is the barrier height as seen from the *trans* configuration; the corresponding barrier height from the *cis* configuration is 5.70±0.71 kcal/mole. The uncertainties in the barrier heights must be interpreted cautiously because they have been calculated assuming the V_4 and higher coefficients to be zero. The most important contribution to the uncertainty in the barrier heights probably comes from the neglect of V_4 and is roughly $-4V_4$.

VI. DISCUSSION

The values of V_1, V_2, and V_3 for cyclopropanecarboxylic acid fluoride are compared to the corresponding values for cyclopropanecarboxaldehyde and acrylyl fluoride in Table X. The values for the aldehyde are from I and the values for acrylyl fluoride were computed by us from data given by Keirns and Curl.[7] It would be very desirable to have the torsional potential constants of acrolein for inclusion in this table. Unfortunately, the microwave spectrum of the species of acrolein with the oxygen atom *cis* to the double bond is either too weak to be observed or is nonexistent.[8] A potential function for liquid acrolein determined by ultrasonic techniques[9] has not been included because it is for the liquid rather than the gas. The absence of a microwave spectrum for *cis* acrolein can be rationalized by a comparison of the V_1 values in Table X. For the cyclopropane compounds the increased stability of the *cis* conformer of the acid fluoride compared to the aldehyde is mainly a result of a much more negative V_1 in the acid fluoride. If a similar difference in V_1 occurs for acrylyl fluoride and acrolein, the value of V_1 for the latter compound would be approximately +1 kcal/mole. This would greatly decrease the stability of the *cis* conformer. Cherniak and Costain have estimated that the ground state of *cis*-acrolein, if it occurs, must lie at least 2.8 kcal/mole above the ground state of the *trans* species.[8] A large positive value of V_1 would lead to this result.

In I we discussed the potential constants of cyclopropanecarboxaldehyde as being the net result of electronic effects of the orbitals of the axial atoms and steric effects of the nonbonded atoms. The steric effects were attributed entirely to interactions between the hydrogen and oxygen atoms of the aldehyde group with two of the out-of-plane CH environments. Similar steric effects are expected for the acid fluoride so that we write

$$V_1{}^S=1.6(V_1{}^{\mathrm{F-CH}}-V_1{}^{\mathrm{O-CH}}),$$

$$V_3{}^S=0.6(V_3{}^{\mathrm{F-CH}}-V_3{}^{\mathrm{O-CH}}),$$

$$V_5{}^S=2.0(V_5{}^{\mathrm{F-CH}}-V_5{}^{\mathrm{O-CH}}),$$

where $V_n{}^S$ is the steric contribution to V_n, and $V_n{}^{\mathrm{F-CH}}$ and $V_n{}^{\mathrm{O-CH}}$ are the differences between the maximum and minimum contributions from the F–CH and O–CH interactions, respectively. The maximum contributions occur at angles of ±35° and ±145° measured from the *trans* configuration, and the signs are such that positive values of $V_n{}^{\mathrm{F-CH}}$ and $V_n{}^{\mathrm{O-CH}}$ indicate repulsion.

As indicated in I the relative values of V_1 and V_3 in the two cyclopropane compounds shown in Table X can be explained by assuming that the interaction between the acyl fluorine atom and the CH environment is more repulsive than the interaction between the aldehyde H atom and the CH region. Cyclopropanecarboxylic acid chloride has been shown by electron diffraction[10] to occur with approximately 85% of the molecules with the oxygen *cis* to the ring. This would be explained here as being the result of a Cl–CH interaction which was more repulsive than the F–CH interaction in the acid fluoride.

A comparison of the V_2 values in Table X shows them to increase in the order: cyclopropanecarboxaldehyde, cyclopropanecarboxylic acid fluoride, acrylyl fluoride. As in I, we ascribe these values to conjugation across

TABLE X. Comparison of torsional potential constants[a] for cyclopropanecarboxylic acid fluoride, cyclopropanecarboxaldehyde, and acrylyl fluoride.

Molecule	V_1	V_2	V_3
Cyclopropanecarboxylic acid fluoride	−1520	5150	990
Cyclopropanecarboxaldehyde	−230	4400	275
Acrylyl fluoride[b]	−2750	7300	185

[a] In calories/mole. The potential constants in this table are defined assuming that the torsional angle is zero in the configuration in which the oxygen atom is *trans* to the ring or to the double bond.

[b] Computed from the data given in Ref. 7 and assuming $F=1.299+0.062\cos\theta$ cm^{-1}.

the CC bond from the CO bond to the ring or to the double bond. The V_2 value for acrylyl fluoride is larger than that of the other two compounds, which is consistent with the expectation that conjugation with a vinyl group should be stronger than with a cyclopropane ring. The V_2 value for cyclopropanecarboxylic acid fluoride is larger than for the corresponding aldehyde, and this is consistent with the fact that the fluorine atom has a lone pair of electrons which could contribute to the conjugation.

The dipole moment of *trans*-cyclopropanecarboxylic acid fluoride is 0.2 D greater than for the *cis* rotamer. In I the 0.5-D difference between the two forms of cyclopropanecarboxaldehyde was attributed to a dipole-moment contribution in the plane of the ring with its negative end toward the axial carbon atom. A similar contribution would explain the difference in the acid fluoride. The smaller *trans–cis* difference in the acid fluoride compared to the aldehyde is apparently the result of a smaller *trans–cis* change in orientation of the COF contribution to the moment compared to the corresponding change for the CHO contribution.

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Magnetothermodynamics of $CuK_2(SO_4)_2 \cdot 6H_2O$. II. Magnetic Moment, Heat Capacity, Entropy from 0.5 to 4.2°K with Fields to 90 kG along the γ Magnetic Axis*

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This is a continuation of our magnetothermodynamic study of a 3.912-cm-diam spherical single crystal of $CuK_2(SO_4)_2 \cdot 6H_2O$. The magnetic moment and heat capacity have been measured over the range 0.5–4.2°K, with fields of 0, 0.5, 1.0, 2.5, 5, 10, 15, 25, 40, 65, and 90 kG directed along the γ magnetic axis. At 0.5°K the magnetic moment reached limiting values in the field range 45–90 kG. $\mathbf{M}_\gamma(\text{limit}) = \mathbf{M}_\gamma(\text{sat}) + \chi_\gamma(\text{dia})\mathbf{H} = 5782.3 - 2.45 \times 10^{-4} H$ G·cm³/mole, where -2.45×10^{-4} is the molal diamagnetic susceptibility, and 5782 is the molal saturation value of the temperature-dependent paramagnetic system. Thus, $g_\gamma = 2.071$. The heat capacities at 90, 65, and 40 kG approached zero below 1°K, thus giving a common zero reference for the entropy of the lattice and electron systems. The heat required to remove quanta of $h/2\pi$ from the saturated condition was slightly larger than the magnetic work $g\beta H$ as expected for a ferromagnetic system. No evidence of hysteresis was observed at temperatures above 0.5°K. Temperature-field measurements on 31 isentropes, which connected the isoerstedic heat capacity series, evaluated the entropy over the experimental range. The total electronic entropy was found to be 1.379 gibbs/mole compared to the expected $R \ln 2 = 1.3775$ gibbs/mole. Smoothed values of the heat capacity, entropy, magnetic moment, enthalpy, internal energy, differential isothermal magnetic susceptibility, differential isoerstedic temperature coefficient of magnetic moment, and the isothermal work of magnetization are tabulated.

This paper reports a continuation of our investigation[1] of a 3.912-cm-diam spherical single crystal of $CuK_2(SO_4)_2 \cdot 6H_2O$. The initial paper presented measurements with the field along the *b* crystallographic axis. In the present work the magnetic field was directed along the γ magnetic axis. The crystal preparation and analysis have been described previously.[1] It had been planned to utilize the same magnetocalorimeter for the entire series of investigations on $CuK_2(SO_4)_2 \cdot 6H_2O$, reorienting and pinning[2] the crystal as necessary. However, failure of the carbon resistance thermometer made it necessary to transfer the sample to an essentially identical apparatus.[3] In the previous experiment,[1] the input of heat due to vibration was much more serious than in any of our other investigations, due presumably to accidentical tuning to some characteristic laboratory frequency. Before the calorimeter was replaced, as mentioned above, the three 15-cm-long support tubes were joined at their midpoints by thin stiff glass fibers, to change the resonant frequency. The horizontal glass fibers, which did not increase the thermal conductivity, were attached by small drops of epoxy to avoid glass