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PART I. THE MICROWAVE SPECTRUM AND RING PUCKERING POTENTIAL OF 1, 1-DIFLUOROCYCLOPENTANE. PART II. COMPUTERS AS INTERACTIVE DEVICES IN CHEMICAL EXPERIMENTS

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PUCKERING POTENTIAL OF
1, 1-DIFLUOROCYCLOPENTANE
PART II. COMPUTERS AS INTERACTIVE DEVICES
IN CHEMICAL EXPERIMENTS

Richard Millikan
(Ph. D. Thesis)

November 1968

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PART I. THE MICROWAVE SPECTRUM AND RING PUCKERING POTENTIAL
OF 1,1 DIFLUOROCYCLOPENTANE

PART II. COMPUTERS AS INTERACTIVE DEVICES IN CHEMICAL EXPERIMENTS

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ABSTRACT

The microwave spectrum of 1,1 difluorocyclopentane has been studied in detail. The rotational spectra for the lowest ten vibrational states have been assigned. Microwave-microwave double resonance techniques have been used extensively in the assignment of two of these states. An analysis of the vibration-rotation interaction present in the spectra has yielded a determination of the potential energy surface governing the out-of-plane motions of the ring-skeletal atoms. The molecule was found to be stably bent with a barrier to pseudorotation of $280 \pm 20 \text{ cm}^{-1}$. An interpretation of the potential in terms of a molecular model for the out-of-plane vibrations has been made. Under the assumptions of this model, it is found that the effective $\text{CH}_2\text{-CF}_2$ torsional barrier is less than the corresponding $\text{CH}_2\text{-CH}_2$ one by at least 80 cm^{-1} .

An interface between a Varian A-60 NMR spectrometer and a small digital computer is described. A number of general aspects of the use of computers as interactive elements in chemical experiments are discussed with relation to our experience.

PART I - THE MICROWAVE SPECTRUM AND RING PUCKERING
POTENTIAL OF 1,1-DIFLUOROCYCLOPENTANE

A. INTRODUCTION

The microwave study of 1,1-difluorocyclopentane was undertaken in order to gain a better understanding of the nature of out-of-plane bending vibrations in small ring compounds and in particular of the effect of small changes in molecular geometry on these motions. As such it is best considered with relation to similar studies on tetrahydrofuran and 2,5-dihydrofuran¹ and also the four-membered rings trimethylene oxide,² trimethylene sulfide³ and 1,1-difluorocyclobutane.⁴

In five-membered rings there are two out-of-plane vibrational modes. In saturated rings particularly, both of these modes, one of which we label a "twist" and the other a "bend," have a low fundamental frequency and a large amplitude and are not in general well described by a harmonic potential. In addition there is the possibility that, if sufficiently nearly degenerate, the two modes may couple to give rise to the phenomenon of pseudorotation.^{5,6} In this case vibrational energy may be transferred around the ring without the molecule's approaching a planar configuration. The "phase" of the ring puckering motion rotates while the amplitude remains nearly constant.

The point of departure for the study of five membered rings is cyclopentane. The symmetry of cyclopentane requires that the bend and twist be degenerate. The molecule almost certainly exhibits free pseudorotation as postulated by Pitzer⁵ to explain entropy data. A recent infrared study⁷ has demonstrated the existence of pseudorotation-like energy levels in cyclopentane. In tetrahydrofuran the symmetry is reduced by the replacement of one methylene group by an oxygen atom. Detailed infrared⁸ and microwave studies⁶ have shown that tetrahydrofuran does exhibit pseudorotation, but that the reduction of the molecular

symmetry from D_{5h} to C_{2v} leads in this case to a small barrier of about 30 cm^{-1} . The purpose of this study is to determine the effect of the replacement of one of the methylene groups of cyclopentane by a CF_2 , both on the molecular conformation and on the dynamics of ring puckering. It is clear that two effects will be in evidence; one the drastic mass change at one point of the ring skeleton, and the other the chemical change due to the difference in size and electron affinity of hydrogen and fluorine substituents. It is hoped that a better understanding of the nature of low frequency ring bending vibrations will result, and also less directly, on understanding of the effect of fluorine substitution on the valence force fields in a variety of molecules.

Microwave spectroscopy has proven to be an exceedingly powerful tool for the analysis of low frequency vibrations in a number of molecules. The quantum mechanical averaging over the vibration of the instantaneous rotational constants leads to a separate set of constants and a separate rotational spectrum for each vibrational energy state. The variation of rotational constants with vibrational eigenstate may be related to expectation values of the vibrational coordinates and thuse to a quantum mechanical model for the skeletal motions. When vibrational levels are very nearly degenerate, perturbations to the normal rigid rotor Hamiltonian may be evaluated to give directly precise vibrational energy splittings. Such effects have previously been observed in a number of molecules and have been of great value in determining the vibrational energy manifold.

This study of 1,1-difluorocyclopentane was begun by Chadwick Tolman. His results are described in detail in reference 9. They are briefly summarized here. The rotational spectra for the ground and first four

excited states were observed and assigned for the parent compound and the 2,2,5,5 tetradeutero analog. Small deviations from the rigid rotor predictions were observed, but were not explained. Approximate relative intensity data showed the first four excited states to lie within about 80 cm^{-1} of the ground state.

The variation in the B and C rotational constants as well as relative intensity data suggested strongly that the vibrational levels occur as nearly degenerate pairs with the degeneracy decreasing with increasing vibration quantum number. This in turn suggests a vibrational motion determined by a double minimum potential with a barrier greater than the energy of the highest observed pair levels. Careful Stark measurements and an analysis of the change in rotational constants with deuterium substitution at the α -positions showed that the molecule cannot be permanently bent. The conclusion was that 1,1-difluorocyclopentane is permanently twisted by about 35° and the vibrational motion about this configuration is nearly pure bending.

The present study represents an attempt to check the previous conclusions and to go beyond them to give a quantitative picture of the out-of-plane motions in this molecule.

B. EXPERIMENTAL

The sample of 1,1 difluorocyclopentane used for all microwave measurements was either that used previously by Chadwick Tolman or one prepared in an identical manner.⁹ It was found to be essentially pure by gas phase chromatography.

The microwave spectra were run on a conventional 5 kc/sec stark modulated spectrometer with phase-locked source.¹⁰ Spectra were taken in the region 8-40 kmc/sec in a 12 foot absorption cell cooled to dry

ice temperature. The use of backward diode detectors¹¹ in the frequency region below about 26 kmc/sec was found to improve signal-to-noise considerably over conventional crystals. A solid state square wave generator with exceptionally flat "off-time" was useful for measurements on a number of lines with very "fast" Stark effect. A few of the weakest absorption lines were measured on a computer-coupled on-line spectrograph^{12,13} using time averaging and digital filtering techniques to increase signal-to-noise. Except where noted frequencies are measured accurate to 0.02 mc/sec.

C. THE SPECTRUM

The microwave spectrum of 1,1 difluorocyclopentane is quite characteristic of a near symmetric prolate top with a-dipole selection rules. No strong Q-branch transitions appear in the region 8-40 kmc/sec. R band transitions ($J \rightarrow J+1$) are observed from $J=1$ to $J=8$. For each rotational transition a large number of vibrational satellites are in evidence, immediate evidence for a dense vibrational energy manifold. These occur in pairs separated by 50-200 mc/sec. The splitting in the strongest pair, assigned to the $v=0,1$ states, was too small to be observed except as a slight broadening of one $J=8 \rightarrow J=9$ line. The next two pairs assigned to $v=2,3$ and $v=4,5$ states showed increasing splittings, the largest being about 5 mc/sec. Spectral lines for these six vibrational states were assigned by Dr. Tolman to a normal rigid-rotor hamiltonian. Small deviations of 1 or 2 mc/sec from the predicted frequencies were observed.

Transitions for the next two vibrational states are in many cases split far enough so as to make their identification by the characteristic doubling impossible. In addition, it became clear relatively early that

these states were not "rigid" - i.e. their spectra could not be characterized by the normal free rotor Hamiltonian $H = AP_A^2 + BP_B^2 + CP_C^2$. Similar behavior has been observed in the spectra of cyanamide¹¹ and a number of ring compounds,^{1,3,4,15} and in these cases was explained by a Coriolis coupling between vibrational angular momentum and the overall rotation of the molecule. The following two sections discuss the vibration rotation hamiltonian. Each rotational transition is seen to be dependent upon eight parameters: the rotational constants for two vibrational states, the energy splitting and the perturbing matrix element. These were all treated as empirical parameters to be determined by the data. Identification on the basis of Stark effect was at best somewhat unsure since the low J lines for these states were very weak and resolution of the many Stark components of the higher J lines was not found to be possible in most cases.

Because of these difficulties, a number of double resonance experiments were undertaken. These are described in a later section. The results of these experiments led to several revisions in assignment. The final unambiguous assignment was found to be quite well represented by our theory (Table II). The vibrational energy splitting is 692 ± 10 mc/sec, or only 0.023 cm^{-1} .

The data described strongly suggest a vibrational motion determined by a double minimum potential, with a barrier above the energy of the $v=6,7$ states. Relative intensity measurements put this energy at $80-130 \text{ cm}^{-1}$ above the ground state. In order to determine the nature of the potential near the barrier, a search was made for transitions assignable to higher vibrational states. Two sets of transitions consistent with a rigid-rotor hamiltonian were found and assigned to the $v=8$ and $v=9$ states. The

Table I

	LABEL	CALC.	EXP.	EXP.-CALC.	PERTURBATION
V =4	2(1,2) - 3(1,3)	12900.65	12901.20	.55	.68
V =5	2(1,2) - 3(1,3)	12901.05	12901.20	.15	1.24
V =4	2(1,1) - 3(1,2)	13348.70	13347.98	-.72	-1.24
V =5	2(1,1) - 3(1,2)	13349.12	13347.98	-1.14	-.68
V =5	2(2,1) - 3(2,2)	13031.21	13031.30	.09	-98.93
V =4	3(0,3) - 4(0,4)	17424.05	17424.20	.15	-.00
V =5	3(0,3) - 4(0,4)	17422.88	17422.91	.03	-.00
V =4	3(1,3) - 4(1,4)	17191.10	17191.30	.20	.31
V =5	3(1,3) - 4(1,4)	17190.87	17191.14	.27	.42
V =4	3(1,2) - 4(1,3)	17788.94	17788.72	-.22	-.42
V =5	3(1,2) - 4(1,3)	17788.71	17788.72	.01	-.31
V =4	3(2,1) - 4(2,2)	17562.78	17562.68	-.10	-20.59
V =5	3(2,1) - 4(2,2)	17568.80	17568.86	.06	-15.41
V =4	4(0,4) - 5(0,5)	21722.26	21722.48	.22	-.01
V =5	4(0,4) - 5(0,5)	21720.16	21720.31	.15	-.01
V =4	4(1,4) - 5(1,5)	21474.74	21474.70	-.04	.16
V =5	4(1,4) - 5(1,5)	21474.19	21474.20	.01	.20
V =4	4(1,3) - 5(1,4)	22218.61	22218.63	.02	-.20
V =5	4(1,3) - 5(1,4)	22217.94	22218.15	.21	-.16
V =4	4(3,2) - 5(3,3)	21911.12	21911.13	.01	1.39
V =5	4(3,2) - 5(3,3)	21911.26	21911.36	.10	1.38
V =4	4(3,1) - 5(3,2)	21914.57	21914.28	-.29	-1.38
V =5	4(3,1) - 5(3,2)	21914.88	21914.56	-.32	-1.39
V =4	4(4,0) - 5(4,1)	21902.40	21902.30	-.10	-.02
V =5	4(4,0) - 5(4,1)	21902.54	21902.30	-.24	.01
V =4	5(0,5) - 6(0,6)	25990.33	25990.45	.13	-.01
V =5	5(0,5) - 6(0,6)	25987.17	25987.18	.01	-.01
V =4	5(1,5) - 6(1,6)	25750.67	25750.45	-.21	.09
V =5	5(1,5) - 6(1,6)	25749.78	25749.63	-.15	.11
V =4	5(1,4) - 6(1,5)	26634.54	26634.47	-.07	-.11

Table I (continued)

	LABEL	CALC.	EXP.	EXP.-CALC.	PERTURBATION
V =5	5(1,4) - 6(1,5)	26633.28	26633.50	.22	-.09
V =4	5(2,4) - 6(2,5)	26227.37	26227.66	.29	4.80
V =5	5(2,4) - 6(2,5)	26227.37	26227.66	.29	5.48
V =4	5(2,3) - 6(2,4)	26487.04	26487.24	.20	-5.47
V =5	5(2,3) - 6(2,4)	26490.01	26489.69	-.32	-4.79
V =4	5(3,3) - 6(3,4)	26303.10	26303.42	.32	4.09
V =5	5(3,3) - 6(3,4)	26302.56	26302.40	-.16	3.31
V =4	5(3,2) - 6(3,3)	26312.16	26312.83	.67	-3.31
V =5	5(3,2) - 6(3,3)	26312.05	26312.13	.08	-4.09
V =4	6(0,6) - 7(0,7)	30232.39	30232.40	.01	-.01
V =5	6(0,6) - 7(0,7)	30228.25	30228.16	-.09	-.01
V =4	6(1,6) - 7(1,7)	30018.58	30018.20	-.38	.06
V =5	6(1,6) - 7(1,7)	30017.32	30017.06	-.26	.06
V =4	6(1,5) - 7(1,6)	31032.53	31032.36	-.17	-.07
V =5	6(1,5) - 7(1,6)	31030.39	31030.74	.35	-.06
V =4	6(2,5) - 7(2,6)	30574.22	30573.70	-.52	2.29
V =5	6(2,5) - 7(2,6)	30573.34	30573.70	.36	2.48

Table II

	LABEL	CALC.	EXP.	EXP.-CALC.	PERTURBATION
V =6	2(1,2) - 3(1,3)	12948.45	12948.35	-.10	15.39
V =7	2(1,1) - 3(1,2)	13360.13	13359.73	-.40	-15.40
V =6	3(1,3) - 4(1,4)	17245.88	17245.90	.02	10.49
V =7	3(1,3) - 4(1,4)	17295.99	17296.12	.13	62.59
V =6	3(1,2) - 4(1,3)	17761.53	17761.46	-.07	-62.62
V =6	4(1,4) - 5(1,5)	21537.88	21537.89	.01	6.87
V =7	4(1,4) - 5(1,5)	21550.46	21550.25	-.21	22.89
V =6	4(1,3) - 5(1,4)	22240.44	22240.68	.24	-22.95
V =7	4(1,3) - 5(1,4)	22253.70	22253.90	.20	-6.94
V =6	4(3,2) - 5(3,3)	21957.62	21957.61	-.01	1.48
V =7	4(3,2) - 5(3,3)	21959.81	21959.77	-.04	1.98
V =6	4(3,1) - 5(3,2)	21959.78	21959.77	-.01	-1.92
V =7	4(3,1) - 5(3,2)	21962.94	21963.05	.11	-1.41
V =6	4(4,0) - 5(4,1)	21948.85	21948.54	-.31	-.06
V =7	4(4,0) - 5(4,1)	21950.30	21950.47	.17	.05
V =6	5(0,5) - 6(0,6)	26062.35	26062.85	.50	-.64
V =7	5(0,5) - 6(0,6)	26044.02	26043.75	-.27	-.78
V =6	5(1,5) - 6(1,6)	25823.66	25823.51	-.15	4.51
V =7	5(1,5) - 6(1,6)	25824.42	25824.46	.04	10.59
V =6	5(3,3) - 6(3,4)	26358.39	26357.80	-.59	4.11
V =7	5(3,3) - 6(3,4)	26361.60	26361.30	-.30	5.02
V =6	5(3,2) - 6(3,3)	26364.11	26365.30	1.19	-4.91
V =7	5(3,2) - 6(3,3)	26369.85	26370.20	.35	-3.99
V =6	5(4,2) - 6(4,3)	26344.17	26344.00	-.17	-.06
V =7	5(4,2) - 6(4,3)	26346.49	26346.80	.31	.19
V =6	5(5,0) - 6(5,1)	26336.64	26336.40	-.24	-.03
V =7	5(5,0) - 6(5,1)	26338.21	26338.55	.34	.04
V =6	6(0,6) - 7(0,7)	30319.32	30318.76	-.56	-.80
V =7	6(0,6) - 7(0,7)	30295.05	30294.83	-.22	-.94
V =6	6(1,6) - 7(1,7)	30102.50	30102.16	-.34	3.00
V =7	6(1,6) - 7(1,7)	30097.67	30098.01	.34	5.72
V =6	7(0,7) - 8(0,8)	34557.48	34557.73	.25	-.86
V =7	7(0,7) - 8(0,8)	34528.89	34528.91	.02	-.96

Table III

$V = 8$

Transition	Experimental	Calculated	Exp. - Calc.
4(0,4) - 5(0,5)	21851.28	21850.56	0.72
4(4,0) - 5(4,1)	21991.79	21991.92	-0.13
5(0,5) - 6(0,6)	26157.05	26156.98	0.07
5(4,1) - 6(4,2)	26394.70	26394.77	-0.07
5(5,0) - 6(5,1)	26388.40	26388.53	-0.13
6(0,6) - 7(0,7)	30437.04	30437.84	-0.80
6(4,3) - 7(4,4)	30800.19	30799.97	0.22
6(4,2) - 7(4,3)	30800.19	30800.49	-0.30
6(5,1) - 7(5,2)	30790.45	30790.36	0.09
6(6,0) - 7(6,1)	30784.78	30784.87	-0.09
7(0,7) - 8(0,8)	34697.83	34697.50	0.33
7(4,3) - 8(4,4)	35209.30	35209.24	0.06
7(4,4) - 8(4,5)	35207.61	35207.82	-0.21
7(5,2) - 8(5,3)	35194.12	35193.91	0.21
7(6,1) - 8(6,2)	35186.05	35185.90	0.15
7(7,0) - 8(7,1)	35180.19	35180.22	-0.03

A = 4616.15

B = 2270.60

C = 2125.10

$D_{JK} = -0.004$

$D_{JJ} = -0.001$

Table IV

V = 9

Transition	Experimental	Calculated	Exp. - Calc.
4(0,4) - 5(0,5)	21773.05	21773.16	-0.11
4(4,0) - 5(4,1)	22002.03	22002.02	0.01
5(0,5) - 6(0,6)	26043.75	26043.62	-0.13
6(0,6) - 7(0,7)	30296.30	30296.34	-0.04
6(5,2) - 7(5,3)	30805.70	30805.69	0.01
6(6,0) - 7(6,1)	30797.16	30797.14	0.02
7(5,3) - 8(5,4)	35214.60	35214.57	0.03
7(5,2) - 8(5,3)	35214.60	35214.78	-0.18
7(6,1) - 8(6,2)	35202.14	35201.79	0.25
7(7,0) - 8(7,1)	35194.12	35194.26	-0.14

$$A = 3419.43$$

$$B = 2265.44$$

$$C = 2130.25$$

$$D_{JK} = -0.001$$

$$D_{JJ} = -0.003$$

Table V Observed Rotational Constants

	A		B		C	
$v=0,1$	4175.8 ± 2	mc/sec	$2250.57 \pm .02$	mc/sec	$2096.36 \pm .02$	mc/sec
$v=2$	4175.4 ± 2	mc/sec	$2259.73 \pm .02$	mc/sec	$2107.55 \pm .02$	mc/sec
$v=3$	4177.0 ± 2	mc/sec	$2259.73 \pm .02$	mc/sec	$2107.54 \pm .02$	mc/sec
$v=4$	4189.5 ± 5	mc/sec	$2263.41 \pm .03$	mc/sec	$2113.31 \pm .03$	mc/sec
$v=5$	4163.6 ± 5	mc/sec	$2263.41 \pm .03$	mc/sec	$2113.29 \pm .03$	mc/sec
$v=6$	4249.8 ± 5	mc/sec	$2267.08 \pm .03$	mc/sec	$2119.39 \pm .03$	mc/sec
$v=7$	4101.2 ± 5	mc/sec	$2267.19 \pm .05$	mc/sec	$2119.16 \pm .03$	mc/sec
$v=8$	4616 ± 20	mc/sec	$2270.60 \pm .05$	mc/sec	$2125.10 \pm .05$	mc/sec
$v=9$	3441 ± 20	mc/sec	$2265.90 \pm .05$	mc/sec	$2129.63 \pm .05$	mc/sec
$\Delta E (4,5) =$			$\alpha_{1a} \langle 4 P_1 5 \rangle =$			
$\Delta E (6,7) = 632.0 \pm 10$	mc/sec		$\alpha_{1a} \langle 6 P_1 7 \rangle = 234.2$	5.		

E. VIBRATION ROTATION INTERACTION

When there are vibrations and rotations of comparable frequency in a molecule, the two motions may couple and the full interaction Hamiltonian,

$$H = H_r + H_v + H_{rv}$$

must be considered. In its most general form this Hamiltonian may be written as:

$$H_r = \sum_i \sum_j P_i \cdot P_j \cdot (I^{-1})_{ij}$$

$$H_v = \sum_l \sum_k 1/2 p_l \cdot p_k \cdot (\mu^{-1})_{lk} + V(q_l, q_k)$$

$$H_{rv} = \sum_i \sum_l \alpha_{il} P_i \cdot p_l$$

The indices i, j run over the spatial coordinates x, y, z ; l, k run over the normal vibrational modes. P_i is the rotational angular momentum about i ; p_l is the vibrational linear momentum conjugate to the coordinate q_l . α is a structural term relating the vibrational linear and angular momenta. As discussed in the previous section, the requirement that this Hamiltonian belong to the totally symmetric representation of the molecular point group may eliminate many of these terms. Others may be removed with a particular choice of axes. For our calculations the instantaneous inertial axes were used. Considering only the out-of-plane vibrational modes as coupling appreciably with rotation, the rotational part of this Hamiltonian becomes:

$$H = (AP_a^2 + BP_b^2 + CP_c^2) + \sum_{i=a,b,c} \alpha_{ia} p_1 \cdot P_i + \sum_{i=a,b,c} \alpha_{2b} p_2 \cdot P_i$$

where p_1 and p_2 are the linear momenta of the twist and bend modes

respectively. It should be noted that the rotational constants are functions of q_1 and q_2 .

In the basis set where H_r and H_v are diagonal, the final two terms are off-diagonal in twist and bend vibrational states respectively. If all vibrational splittings are much greater than the rotational energy differences, these terms may be removed by a second order perturbation treatment yielding a small correction to the A and B rotational constants.¹⁴ Such conditions are usually trivially small in microwave spectroscopy. If, however, vibrational near degeneracies exist — a situation to be expected in double (or more) minimum problems — these terms must be treated explicitly. It should be noted that in the limit of exact vibrational degeneracy, the matrix elements ($v/P_{vib}/v'$) go to zero in such a way that the perturbation vanishes.¹⁵ Thus it is only in the intermediate range where vibrational and rotational splittings are of the same order that large perturbations to the "rigid" spectrum are to be expected.

In 1,1-difluorocyclopentane the first two pairs of levels showed no Coriolis perturbations of the type described above, though there were small deviations from rigid rotor assignments of some high J lines due to centrifugal distortion. The next several states however, showed definite perturbations attributable to a $P_{V_a}P_a$ coupling term. The assignments of these states is discussed in Section IC. In the calculation of these assignments only one vibrational splitting is treated explicitly; the corrections due to all other terms are absorbed into the rotational constants. Thus eight independent parameters — six rotational constants, the vibrational splitting and the magnitude of the perturbing matrix element — are required to determine the rotational spectra for the two states. An iterative procedure like that discussed in reference 15 was

used to fit the observed transitions to these parameters. Figures 1 and 2 show a portion of the vibronic energy manifold for the $v=4,5$ and $v=6,7$ systems showing schematically the interactions causing the strongest perturbations.

As discussed in Section IG, analysis of the variation of rotational constants with vibrational state allows at best a determination of only the shape of the vibrational potential. Coriolis interactions as discussed above yield absolute energy separations and may give a much more accurate potential scale factor than intensity measurements, as well as information on the shape.

F. DOUBLE RESONANCE EXPERIMENTS

A number of experimenters have shown that microwave-microwave double resonance experiments may be of great assistance in the assignment of complex spectrum.^{4,16-18} Particularly when there is a question as to which of several vibrational states a transition belongs, and consequently Stark effect measurements are of no use in assignment (the Stark effect of a given rotational transition is usually quite similar in different vibrational states), these experiments, if successful, can be decisive in assignment. Such was the case in the assignment of the $v=6,7$ spectrum of 1,1-difluorocyclopentane.

In microwave-microwave double resonance, one rotational transition is irradiated at high power. The normal microwave spectrum of only the transitions with an energy level in common with the pumped transition will be affected. In our experiments the pumping klystron was frequency modulated, creating a population modulation of the upper and lower levels of the irradiated transition. Only transitions involving one of these levels then could be detected by phase sensitive detection.

In practice a small (5-20 V) 5 kc/sec square wave was applied to the reflector of the pumping klystron while its "zero-volt" frequency was slowly swept mechanically. The observing klystron was phased-locked, but not swept. The experimental arrangement was similar, though not identical, to that used by previous experimenters. The pumping klystron was operated at lower frequency and at opposite ends of the absorption cell from the observing source. It was usually operated at maximum power (100 to 700 mw). The high power was decoupled from the detection diode by a high directivity direction coupler and a section of waveguide just too small to pass the lower frequency. It was found very important to isolate the detector ground from that of the klystron by introducing a Mylar spacer in the plumbing. The generation of harmonics of the pumping frequency must be avoided as much as possible as they will pass the waveguide filter. In particular it was found that removal of the crystal used to monitor the pumping source's frequency decreased the problem of "hills" (frequency dependent modulation of the power reaching the detector which is independent of the presence of a sample). Introduction of a tunable band-pass filter⁴ in series with the cut-off filter was also occasionally useful. Figure 3 shows a diagram of the experimental arrangement.

Despite the precautions taken, the presence of "hills" was at times a severe drawback, requiring repeated experiments with and without sample. The intensity of the double resonance transition was found to be a sensitive function of pressure and pumping power. Absolute power was not continuously monitored, and the following remarks are intended only to give a qualitative picture of some observed effects. Figure 4 shows the $v=6 \ 3(1,2) - 4(1,3)$ (---) $4(1,3) - 4(1,4)$ transition as a function

of pressure. The pumping power in this case was fairly low (ca. 100 mw), and the decrease in intensity with increasing pressure is explained as a decrease in the degree of saturation along with an increasing line width. At constant pressure and low pumping power an increase in power increases line intensity, but also shortens the lifetime of the states bounding the transition causing an increase in linewidth both in the pumping and observing frequency domains. In practice it was found that at powers around 1/2 watt, there was little decrease in the intensity of the double resonance transition as the observing klystron was moved as far as 5 mc/sec from the line center. On some of the stronger transitions, however, it was found possible to reduce power sufficiently to obtain resolution of less than 1 mc/sec. Figure 5 shows the transitions $v=6$ and $v=7$ $4(1,4) - 5(1,5) \leftrightarrow 5(1,5) - 6(1,6)$. The results show conclusively that the transition line at 26023.51 is connected to one near 21550 and that the line at 26024.46 is connected to one near 21538. This experiment led to an important revision in assignment for the $v=6$ and $v=7$ states.

The spectra in Fig. 6 suggest strongly that both the lines previously observed at 30294.83 mc/sec and 30296.30 mc/sec are coupled to a transition line near 26043. This was given further credence in a subsequent experiment showing a connection between 26043.75 and both 21767 and 21772 mc/sec. These experiments gave the first clue in the assignment of the $v=9$ state.

Table VI lists the double resonances observed. These experiments were crucial in the assignment of the highly perturbed $v=6,7$ states, and gave valuable clues to the correct assignment in other states.

Table VI

Observed Double Resonance Transitions

$V = 4,5$	$5(1,5) - 6(1,6) \longleftrightarrow 6(1,6) - 7(1,7)$
$V = 4,5$	$5(2,4) - 6(2,5) \longleftrightarrow 6(2,5) - 7(2,6)$
$V = 6$	$3(1,3) - 4(1,4) \longleftrightarrow 4(1,4) - 5(1,5)$
$V = 7$	$3(1,3) - 4(1,4) \longleftrightarrow 4(1,4) - 5(1,5)$
$V = 6$	$3(1,2) - 4(1,3) \longleftrightarrow 4(1,3) - 5(1,4)$
$V = 6$	$4(0,4) - 5(0,5) \longleftrightarrow 5(0,5) - 6(0,6)$
$V = 7$	$4(0,4) - 5(0,5) \longleftrightarrow 5(0,5) - 6(0,6)$
$V = 7$	$5(0,5) - 6(0,6) \longleftrightarrow 6(0,6) - 7(0,7)$
$V = 6$	$5(1,5) - 6(1,6) \longleftrightarrow 6(1,6) - 7(1,7)$
$V = 7$	$5(1,5) - 6(1,6) \longleftrightarrow 6(1,6) - 7(1,7)$
$V = 9$	$4(0,4) - 5(0,5) \longleftrightarrow 5(0,5) - 6(0,6)$

G. POTENTIAL FUNCTION

The primary objectives of this research are first a determination of the potential function governing the out-of-plane vibrations in 1,1-difluorocyclopentane and an understanding of the dynamics of the ring puckering motions, and second, an interpretation of this potential in terms of molecular structure and individual force fields in the molecules. This section discusses the potential while the next relates this to a molecular model.

Before writing down explicit formulae, it might be well to discuss briefly the types of potentials and molecular motions that might be expected — and which must therefore be able to be treated by our theory — in light of what is known of similar molecular systems.

The stable conformation, and vibrational motion about this structure, in ring compounds is largely dependent on the balance of two kinds of internal strains: one, the torsional forces between adjacent substituents and in some cases non-bonding electron clouds, and the other, the force due to bending about the skeletal atoms. Puckering of the ring decreases the torsional strain by allowing the substituent atoms to move away from their planar eclipsed positions; at the same time it decreases the average bond angle. In four membered rings where the ring angles are already quite strained in the planar configuration, the two forces are fairly closely balanced in the unbent ring. All of these molecules so far studied have shown a barrier to the planar configuration, of between 30 and 400 cm^{-1} . The ring angles in 5 membered rings are not highly strained in the unpuckered ring; the torsional forces may, however, be quite large. Consequently it is expected that there will be large potential barrier to the planar configuration. Semi-empirical calculations like those

described in the next section have been made for a number of molecules; all have shown a barrier of around 1000 cm^{-1} . The exception to this would be in case of the introduction of a double bond into the ring, decreasing the torsional strain to the point where the planar configuration may indeed be the most stable. Microwave studies on dihydrofuran¹ and cyclopentane¹⁹ have shown that the former is planar while the latter is bent with a barrier of $250\text{-}500\text{ cm}^{-1}$ to the planar configuration. In rings of six atoms, both the torsional and bending constraints favor a puckered ring and the energy barrier at the planar configuration is typically several thousand cm^{-1} .

There are two out-of-plane vibrational modes in five membered rings and the deviation from planarity is distributed among them. In Fig. 8 are shown a number of possible potentials governing the out-of-plane motions. All have high central barriers and all are characteristic of molecules with at least C_{2v} symmetry in their planar configuration, but they differ remarkably in other respects. Figure 8a shows the potential for the symmetrical cyclopentane. Not only are the twist and bending motions degenerate, but there is a path of zero energy between the two configurations. This is the pseudorotation path. Figure 9 is reproduced from reference 9 to show the relation between the pseudorotation angle and the individual motions of the atoms.

Figure 8b shows the effect of removing the degeneracy of the bend and the twist, but only slightly. There is now a small barrier to pseudorotation, but the motion is essentially similar to that of cyclopentane. This is similar to the potential observed for tetrahydrofuran. In Fig. 8c the two modes are no longer closely degenerate and the motion is nearly pure bending about a permanently twisted conformation. There is no

inherent reason why the potential minimum must occur either at the purely bent or purely twisted configuration with respect to the unique axis. Figure 8d shows a potential in which there are four minima off the axes. This corresponds to nearly degenerate, but completely uncoupled bend and twist.

In order to talk quantitatively about the vibrational potential, this potential must be expressed in some sort of mathematical form. This form must have the capability of describing all the types of potentials described above. A convenient choice is a truncated Taylor series expansion in the out-of-plane coordinates q_1 and q_2 . This is certainly not the only possible choice, but it is an easy one to handle. Past experience with both four and five membered rings has shown that inclusion of terms up to fourth power in the coordinates should be sufficient to describe quite well the molecular dynamics and the available microwave data. It should be noticed that such a potential, although simple, allows each uncoupled mode to have a single minimum or two minima separated by a barrier which may be continuously varied, and allows for variable coupling between the modes. Gaussian barriers have also been used for double minimum problems, but in most cases have not given significantly better results than the simpler power series expansions.

The Hamiltonian becomes:

$$H = \frac{p_1^2}{2M_1} + \frac{p_2^2}{2M_2} + a_1 q_1^2 + a_2 q_2^2 + b_1 q_1^4 + b_2 q_2^4 + c_{12} q_1^2 q_2^2$$

If q_1 and q_2 are the vibrational normal coordinates, cross terms of the form $p_1 p_2 / \mu_{12}$ are zero.²⁰ M_1 and M_2 are not in general independent of the coordinates q_1 and q_2 . Since this dependence is not known, and would require a minimum of two additional terms in the Hamiltonian to be

treated explicitly, we assume that the reduced masses for the vibration are constant. This assumption is valid for the description of energy states for which q_1 and q_2 are fairly well limited close to their equilibrium values. Such should be the case for energy levels well below the barrier, and so we may expect a fairly accurate representation of the first eight or ten levels of 1,1-difluorocyclopentane.

Most of the calculations were done on this form of Hamiltonian, but it is useful for purposes of visualization to make a change of variables. As shown in reference 6, the set of transformations

$$\begin{aligned} X_1 &= q_1 (M_1)^{1/2} & X_2 &= q_2 M_2^{1/2} \\ r \cos \theta &= X_1 & r \sin \theta &= X_2 \end{aligned}$$

lead to the Hamiltonian:

$$\begin{aligned} H &= \frac{1}{r} P_r r^2 P_r \frac{1}{r} + a'_1 r^2 + b'_1 r^4 \\ &+ \frac{1}{r^2} P_\theta^2 + \frac{1}{2}(1-\cos 2\theta)[r^2(a'_2 - a'_1) + r^4(b'_2 - b'_1)] \\ &+ \frac{1}{8}(1-\cos 4\theta)[r^4(c'_{12} - b'_1 - b'_2)] \end{aligned} \quad (2)$$

The primed force constants are $a'_1 = m_1 a$, $b'_1 = m^2 b'$; $c'_{12} = m_1 m_2 c_{12}$. The possibility of the separation of the molecular motion into a radial and a pseudorotation coordinate is clear. In cyclopentane, under the assumption of a high central barrier in which case the two modes separate well, this reduces to two one dimensional Hamiltonians:

$$\begin{aligned} H_r &= \frac{1}{r} P_r r^2 P_r \frac{1}{r} + a'_1 r^2 + b'_1 r^4 \\ H_\theta &= B P_\theta^2 & B &= \langle 1/r^2 \rangle \end{aligned}$$

The pseudorotation energy levels are just those of the free one-dimensional

rigid rotor. Small deviations from the symmetry of cyclopentane will require the addition of the $(1-\cos 2\theta)$ and $(1-\cos 4\theta)$ terms to H_0 . Larger deviations require a complete solution of the two dimensional Hamiltonian. In the case of 1,1 difluorocyclopentane, the vast difference in reduced mass for the bend and the twist led us to the belief that a solution in terms of q_1 and q_2 would be as simple as one in r and θ .

It should be said that the same transformation may be made for the potential as in (2) without the initial transformation to mass reduced units yielding:

$$V = a_1 r^2 + b_1 r^4 + \frac{1}{2} (1-\cos 2\theta) [r^2 (a_2 - a_1) + r^4 (b_2 - b_1)] \quad (3)$$

$$+ \frac{1}{8} (1-\cos 4\theta) [r^4 (c_{12} - b_1 - b_2)]$$

Though not of use for calculations this is a convenient form of the potential for visualization of the actual motions of the molecular frame.

In several past microwave studies on ring compounds it was found possible to determine the potential, within a constant scale factor, without making any assumptions on the actual nature of the motion, by an analysis of the variation of rotational constants with vibrational state. Each rotational constant may be expanded as a Taylor series in the expectation values of the vibrational coordinates, i.e. for two modes

$$A_{\nu\nu} = A_0 + \alpha_{20} \langle q_1^2 \rangle_{\nu\nu} + \alpha_{02} \langle q_2^2 \rangle_{\nu\nu} + \alpha_{40} \langle q_1^4 \rangle_{\nu\nu} + \alpha_{22} \langle q_1^2 q_2^2 \rangle_{\nu\nu}$$

$$+ \alpha_{04} \langle q_2^4 \rangle_{\nu\nu} + \dots \quad (4)$$

Truncating the series at a convenient point (usually at the fourth power in the coordinates), it is possible using an iterative procedure, to calculate the potential which best fits the set of observed rotational

constants. This procedure depends for its success upon the sensitivity of the expectation values of the coordinates to small changes in the potential function. Expectation values are typically sensitive to small changes in potential only for vibrational states rather close to the barrier.

In 1,1-difluorocyclopentane, the quite regular variation of the B and C rotational constants and the indeterminacy of A suggested that such an approach would be of little use. The variation in rotational constants will be used in conjunction with other data in determining the potential, but a unique solution based just on the criteria of (4) is not possible. The other useful data from our experiments is the observed splittings between the $v=4$ and 5 and $v=6$ and 7 vibrational states of 116.6 ± 5 mc/sec and 692.0 ± 10 mc/sec respectively. These two pieces of data are, however, not sufficient to determine the constants in (1) without any assumptions.

The procedure used was as follows: The Hamiltonian was first put in the reduced form²⁶

$$H = S_1(P_1^2 - X_1^2 + \gamma X_1^4) + S_2(P_c^2 - X_2^2 + \gamma X_1^2) + cX_1^2 X_2^2 \quad (5)$$

The transformations are:

$$X' = (2ma)^{1/4} X \quad P' = (1/2ma)^{1/4} P$$

where the primes are left off for convenience in the resultant Hamiltonian. Initial guesses at the five parameters determining the energy were made based upon the model calculations of the next section. The two separate anharmonic oscillator problems were solved in harmonic oscillator basis. Sixty basis functions were used; using the C_{2v} symmetry of the Hamiltonian the problem was factored into that of the diagonalization of four 30×30

matrices. The matrices for x_1^2 and x_2^2 were calculated and transformed to the representation of the anharmonic oscillators. The matrix of the direct product of the two anharmonic oscillators was then calculated, the coupling terms were added, and it was diagonalized to yield the final energies. To yield reasonably accurate energies it was found necessary to include 24 basis functions of the bending mode and 20 of the twist. Symmetry reduced the problem to that of the diagonalization of four 120x120 matrices. The entire problem required about 8 minutes of computer time on a CDC 6600.

This procedure was followed for a number of values of the parameters. It was found, not surprisingly, that the magnitude of the splitting between the pairs of levels was very sensitive to the difference in potential between bent and twisted forms; in terms of Eq. (3) this is just twice the coefficient of the $(1-\cos 2\theta)$ term and may be termed "the barrier to pseudorotation," or more correctly the "twofold barrier." In terms of the reduced Hamiltonian (5), the barrier is $1/4(S_1/\gamma_1 - S_2/\gamma)$. These splittings were much less sensitive to other details of the potential. The barrier consistent with the observed energy differences was found to be $280 \pm 20 \text{ cm}^{-1}$.

Also of some interest is the four-fold barrier; i.e. twice the coefficient of $(1-\cos 4\theta)$ in (3). Calculations showed that the ratio of the $v=4,5$ to the $v=6,7$ splittings, as well as the expansions of B and C rotational constant, is particularly sensitive to this term while being remarkably unaffected by other potential parameters. These data require that the term $(c_{12} - b_1 - b_2)$ in (3) be $-6.6 \pm 2 \times 10^4$. This corresponds to a four-fold barrier of $-73 \pm 20 \text{ cm}$.

A contour drawing of the potential:

$$V = 10^4 (-3.75 q_1^2 - 3.32 q_2^2 + 27.8 q_1^4 + 27.8 q_1^4 + 27.8 q_2^4 + 49.0 q_1^2 q_2^2)$$

is shown in Fig. 10. This potential has a two-fold barrier of 283 cm^{-1} at the bent configuration and a four-fold term of -73 cm^{-1} . Using for the reduced masses of the bend and twist 100.3 and 42.3 AMU as calculated in the next section, the energy levels for this potential are shown in Table VIII. The expectation values $\langle q_1^2 \rangle$ $\langle q_2^2 \rangle$ were calculated for the first several vibrational states. For this potential the assumption that the molecular motion may be thought of as nearly pure bending was found to be invalid even for the lowest few vibrational states. $\langle q_1^2 \rangle$ was found to decrease with vibrational state at approximately the same rate that $\langle q_2^2 \rangle$ increased. The B and C rotational constants were expanded as:

$$B = 2150 + 1441 \langle q_1^2 \rangle + 2504 \langle q_2^2 \rangle \text{ mc/sec}$$

$$C = 1980 + 1641 \langle q_1^2 \rangle + 3141 \langle q_2^2 \rangle \text{ mc/sec}$$

Comparison with the experimental rotational constants is shown in Figs. 11 and 12. An expansion for the A rotational constant was not attempted as the behavior in this case indicates that structural effects are less important than angular momenta coupling. In order to include the second order effect of $P_b p_2$ and $P_c p_2$ terms on the B and C rotational constant, the matrix elements $\langle v/p_2/v' \rangle$ were calculated in the energy representation. The perturbation sums showed that the effect of these terms is nearly identical for the lowest 10 or 12 vibrational states.

The matrix elements $\langle v4/p_1/v5 \rangle$ and $\langle v6/p_1/v7 \rangle$ were calculated. The calculated ratio of the two is 0.119. The experimental value is 0.122.

In summary, although a complete determination of the vibrational

potential has not been possible, we now have a good qualitative picture of the potential and the ring puckering dynamics. In addition a determination of the barrier to pseudorotation has been made and yields the value $280 \pm 20 \text{ cm}^{-1}$. The fourfold barrier is $-72 \pm 20 \text{ cm}^{-1}$.

H. THE MOLECULAR MODEL

In order to relate those characteristics of the vibrational potential determined by the microwave data to the actual chemistry of the molecule, it is useful to postulate a model for the molecular motions in terms of individual structural factors and force fields. The overall potential may then be calculated in this model for a number of values of the structural parameters, and compared with the experimental potential.

The general approach has been described elsewhere^{6,9} and so is very briefly related here. The assumption is made that the molecular potential may be expressed as a sum of torsional potentials described by $V_i = t_i(1 - \cos 3\theta_i)$ where θ_i is the angle between the vectors \vec{k}_i and \vec{k}_{i+1} (\vec{k}_i is the vector perpendicular to the plane defined by the three carbon atoms C_{i-1} , C_i , and C_{i+1}), plus a sum of bending potentials defined by $\frac{b}{2}(\alpha_i - \alpha_i^0)^2$ where α_i is the instantaneous angle and α_i^0 is the equilibrium value. It is assumed that all bond lengths remain constant and that the hydrogens and fluorines remain rigidly attached to the ring atoms. Under these assumptions the instantaneous molecular structure may be specified by four internal parameters. Two of these we may take as the bend coordinate Q_2 and the twist Q_1 . The others we shall call S_1 and S_2 . The potential is calculated for a given Q_1 and Q_2 as a sum of torsional and bending energy. S_1 and S_2 are allowed to relax to give a minimum energy. In addition the coordinates of all the

atoms are calculated in a convenience axis system and then transformed to the inertial or other convenient axis systems (in our case it was found useful to minimize the vibrational angular momentum about the A inertial axis by applying the Eckhart condition).²⁷ Derivatives of all coordinates with respect to q_1 and q_2 are calculated. The 5×5 tensor, A, defining the total kinetic energy by

$$2T = (\omega_a \omega_b \omega_c \ v_1 \ v_2) \begin{pmatrix} A \end{pmatrix} \begin{matrix} \omega_a \\ \omega_b \\ \omega_c \\ v_1 \\ v_2 \end{matrix}$$

is calculated. The upper left 3×3 is just the inertial tensor. The vibrational terms are

$$A_{44} = \sum_i \sum_{xyz} m_i \left(\frac{\partial x_i}{\partial q_i} \right)^2 \quad A_{55} = \sum_i \sum_{xyz} m_i \left(\frac{\partial x_i}{\partial q_2} \right)^2$$

$$A_{45} = A_{s4} \sum_i \sum_{xyz} m_i \left(\frac{\partial x_i}{\partial q_1} \right) \left(\frac{\partial x_i}{\partial q_2} \right)$$

the coupling terms between rotation and vibration are of the form

$$A_{14} = \sum_i m_i \left(y_i \frac{\partial z_i}{\partial q_1} - z_i \frac{\partial y_i}{\partial q_1} \right)$$

In order to make the transition to quantum mechanics the kinetic energy must be expressed in terms of momenta rather than velocities. It is easily shown that

$$2T = (P_a P_b P_c \ p_1 \ p_2) \begin{pmatrix} A^{-1} \end{pmatrix} \begin{matrix} P_a \\ P_b \\ P_c \\ p_1 \\ p_2 \end{matrix}$$

The potential V and the matrix A^{-1} are calculated for a wide range of values of q_1 and q_2 . A power series expansion in these coordinates is then carried out for both V and each element of A^{-1} .

To make a valid comparison with the simplified quantum mechanical model already chosen, a number of assumptions must be made about the kinetic energy. The first is that the vibrational problem separates from the rotational one; that the coupling terms in A^{-1} may lead to corrections to rotational energy as discussed in Section IE, but will not cause significant changes in the vibrational energy. The cross term $\mu_{12}p_1p_2$ in the kinetic energy may in theory be eliminated by a change in variables. In practice this term was found to be small enough to neglect. Also the dependence of the vibrational reduced masses of the two modes upon the coordinates was neglected in our calculations. In practice again this dependence was found to be quite small. In order to minimize the error due to this assumption, the reduced masses were calculated for the configuration of lowest energy rather than for the planar molecule.

The vibrational masses were not found to be particularly sensitive to changes in torsional and bending constants. The potential, however, is quite sensitive to small changes. We label the unstrained ring angles as α_1 and define the bending and torsional force constants b_i and t_i as before. The assumption is made that $\alpha_2 = \alpha_3 = \alpha_4 = 109.5^\circ$, $b_3 = b_4 = 1.08$ m dyne Å/rod², $t_2 = t_3 = t_4 = 550$ cm⁻¹. The assumption of tetrahedral angles for all the ring angles except the one at the CF₂ group is probably quite good.²¹ The bending force constant is taken from an analysis of paraffins.²² The torsional barriers are a little higher than those of ethane, but it was found necessary to use these values in

treating tetrahydrofuran.²³ The four undetermined parameters we take as: $(b_1 - b_3)$, $(b_2 - b_3) = (b_5 - b_3)$, $(t_1 - t_2) = (t_5 - t_2)$ and $(\alpha_1 - \alpha_2)$.

We then explore the effect of these on the potential and in particular on the pseudorotation barrier B. Table VII shows a set of approximate derivatives determined from the molecular model program.

To go further from here, it is necessary to use some chemical intuition. We therefore set the following limits upon our undefined parameters:

$$0 < (b_1 - b_2) < 0.2 \frac{\text{mdyne}\overset{\circ}{\text{A}}}{\text{rad}^2} \quad 0 < (b_2 - b_3) < 0.1 \frac{\text{mdyne}\overset{\circ}{\text{A}}}{\text{rad}^2}$$

$$0 < (\alpha_1 - \alpha_2) < 1.5^\circ$$

The great electronegativity of the fluorine atoms is expected to stiffen the spring constants for the nearby ring angles as well as opening up the unique angle. The limits we have set are quite conservative.

Using these inequalities, the derivatives of Table VII and the observed value of B, it is readily derived that the F-H barrier must be less than H-H one by at least 80 cm^{-1} .

This is the picture we have of the internal forces in 1,1-difluorocyclopentane. The low H-F torsional barrier is somewhat surprising since the barriers in $\text{CFH}_2\text{-CH}_3$ and $\text{CF}_2\text{-CH}_3$ are nearly the same as for ethane.²⁴ On the other hand, Luntz has shown the barrier to the planar configuration in 1,1 difluorocyclobutane is 241 cm^{-1} as compared to (ca. 400 cm^{-1}),²⁵ for the unsubstituted cyclobutane. The lower barrier is probably mainly a reflection of the lower H-F vs. H-H torsion in this molecule.

Table VII

$$\frac{\partial B}{\partial(\alpha_1 - \alpha_2)} = +67$$

$$\frac{\partial B}{\partial(b_1 - b_2)} = +234$$

$$\frac{\partial B}{\partial(b_2 - b_3)} = +150$$

$$\frac{\partial}{\partial(t_1 - t_2)} = +2.31$$

Calculated at $\alpha_1 = \alpha_2 = 109.5^\circ$; $b_1 = 1.27$ mdyne $\text{\AA}/\text{rad}^2$

$b_2 = 1.18$ mdyne $\text{\AA}/\text{rad}^2$; $b_3 = 1.08$ mdyne $\text{\AA}/\text{rad}^2$; $t_1 = 470$ cm^{-1}

$t_2 = 550$ cm^{-1}

$B = 264.2$ cm^{-1}

Table VIII. Energy levels of the Hamiltonian

$$H = 0.199p_1^2 + 0.084p_2^2 + 10^4(-3.75q_1^2 - 3.34q_2^2 + 27.8q_1^4 + 27.8q_2^4 + 49.0q_1^2 \cdot q_2^2)$$

V	Energy (cm ⁻¹)
0	0.000000
1	0.000043
2	20.479685
3	20.480126
4	46.669659
5	46.673418
6	75.746567
7	75.769380
8	106.710107
9	106.829351
10	138.467060

I. CONCLUSIONS

This microwave study of 1,1 difluorocyclopentane has allowed a considerable refinement of our picture of the out-of-plane motions in this molecule, and in five membered rings in general. A complete potential determination has not been possible, but a determination of the two-fold and four-fold barriers has been made. They are $280 \pm 20 \text{ cm}^{-1}$ and $72 \pm 20 \text{ cm}^{-1}$. The twisted configuration is most stable.

The barriers have been related to a molecular model in which the total potential is expressed as a sum of individual torsions and bendings. The analysis has allowed limits to be put on the H-F versus H-H torsional barriers in this molecule. The H-F barrier must be at least 80 cm^{-1} less than the H-H.

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PART I - FIGURE CAPTIONS

- Fig. I-1 A portion of the energy manifold for $V = 4,5$. Approximately to scale. Strong perturbations are shown with dotted lines.
- Fig. I-2 A portion of energy manifold for $V = 6,7$. Approximately to scale. Strong perturbations are shown with dotted lines.
- Fig. I-3 Microwave-microwave double resonance spectrograph.
- Fig. I-4 The $V = 6$ $3(1,2) - 4(1,3) \text{ --- } 4(1,3) - 5(1,4)$ Double Resonance Transition as a function of pressure.
- Fig. I-5 The $V = 6$ and $V = 7$ $4(1,3) - 5(1,4) \text{ --- } 5(1,4) - 6(1,5)$ Double Resonance Transition. Observed single resonances are at 21537.89, 21550.25, 26023.51 and 26024.46 mc/sec.
- Fig. I-6 The $V = 7$ and $V = 9$ $5(0,5) 6(0,6) \text{ --- } 6(0,6) - 7(0,7)$ Double Resonance Transition. Observed single resonances are at 26043.75, 30294.83, and 30296.30 mc/sec.
- Fig. I-7 Approximate structure for 1,1-difluorocyclopentane.
 α is the twist angle; β is the bend angle.
- Fig. I-8 Contour diagrams for a number of possible potential surfaces, (see text).. 100 cm^{-1} contours.
- Fig. I-9 The cyclopentane symmetries.
- Fig. I-10 Contour diagram for the potential
$$V = 10^4 (-3.75 q_1^2 - 3.32 q_2^2 + 27.8 q_1^4 + 27.8 q_2^4 + 49.0 q_1^2 \cdot q_2^2)$$

Fig. I-11 Expansion of B rotational constant. The line indicates calculated expansion. The circles are the experimental values.

Fig. I-12 Expansion of C rotational constant. The line indicates calculated expansion. The circles are the experimental values.

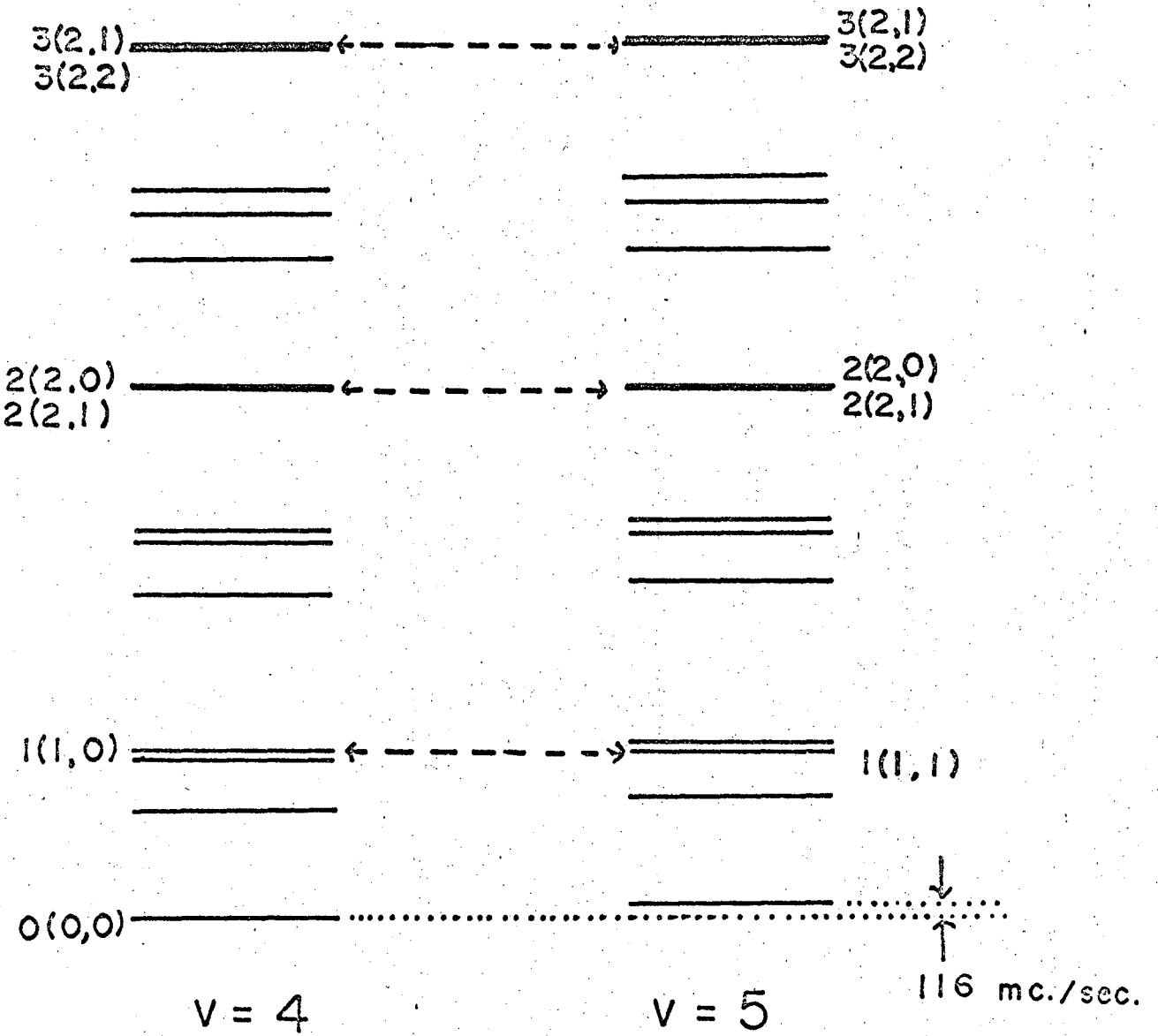
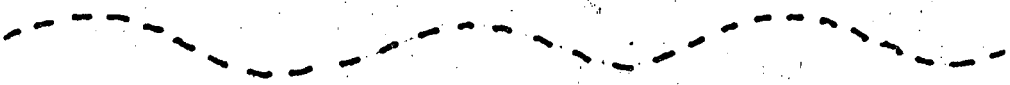


Fig. I-1

4(2,2) ←-----→ 4(2,3)

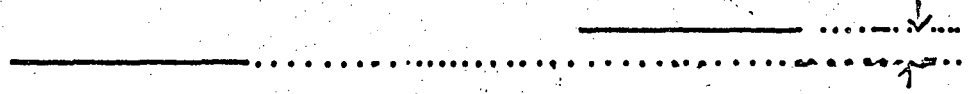


3(2,1) ←-----→ 3(2,2)

3(1,2) ←-----→ 3(1,3)

2(1,1) ←-----→ 2(1,2)

1(1,0) ←-----→ 1(1,1)



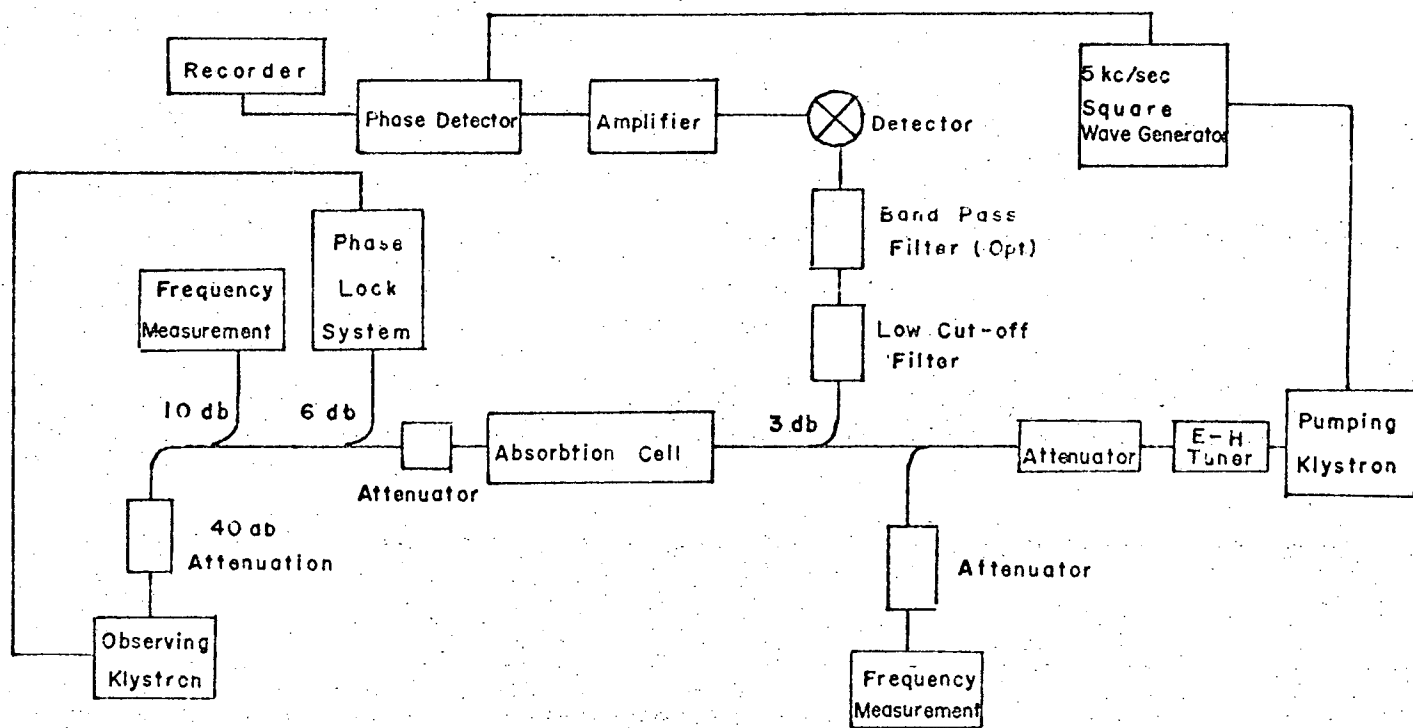
$v = 6$

$v = 7$

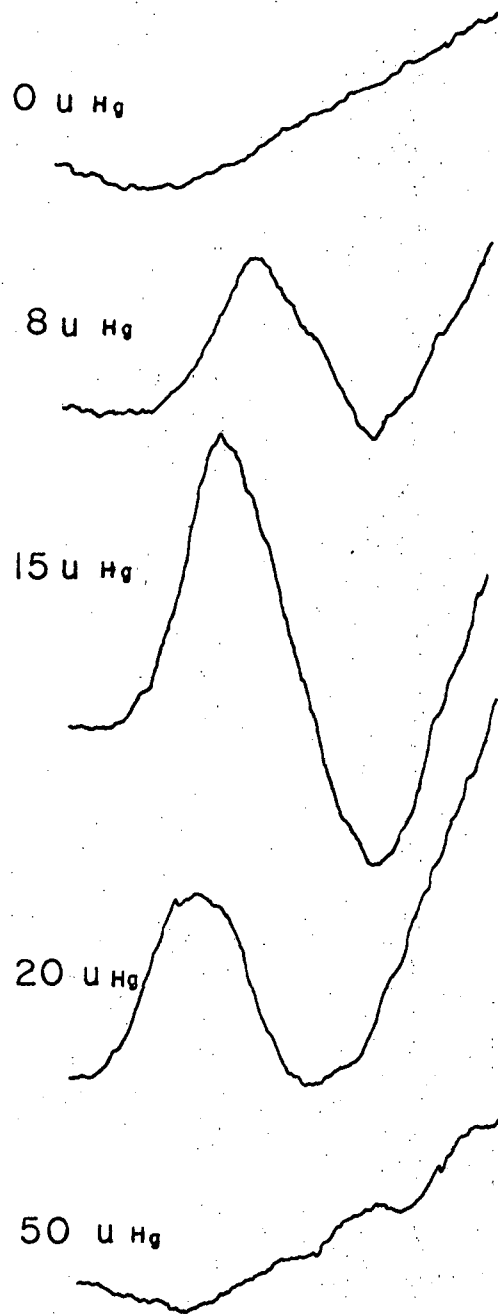
692 mc./sec.

Fig. I-2

Fig. I-3



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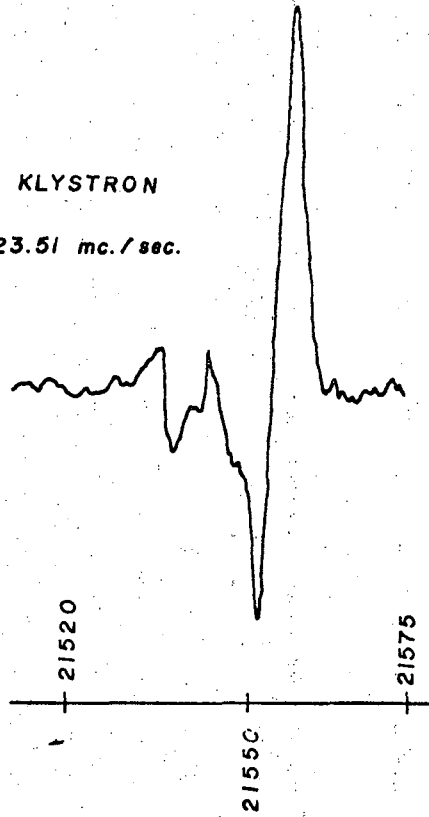


XBL 6811-6172

Fig. I-4

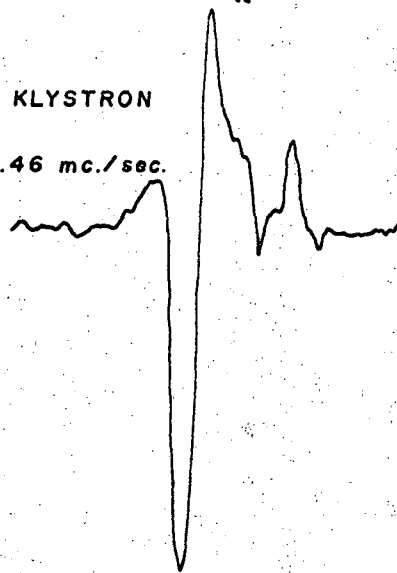
OBSERVING KLYSTRON

25823.51 mc./sec.



OBSERVING KLYSTRON

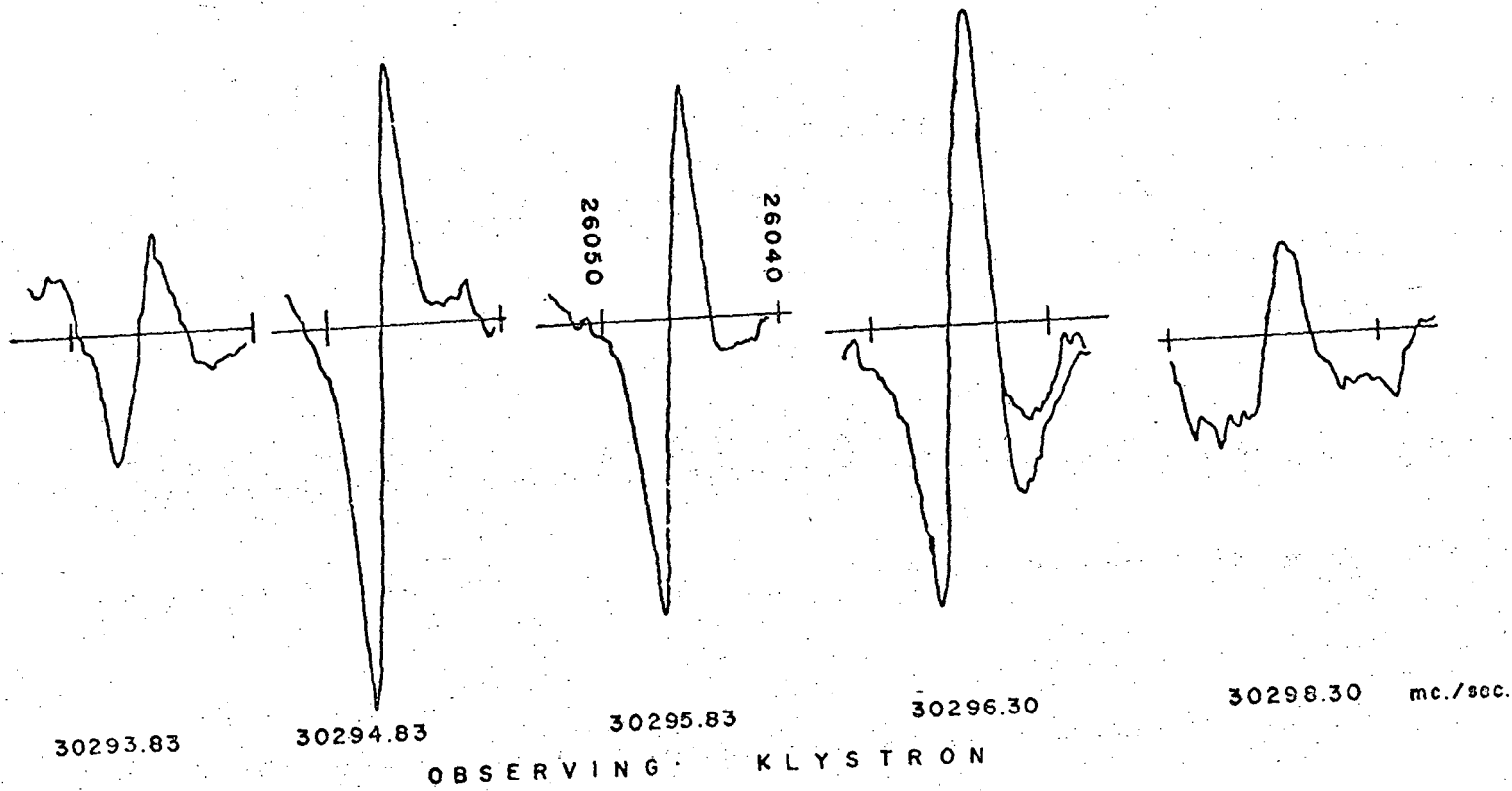
25824.46 mc./sec.



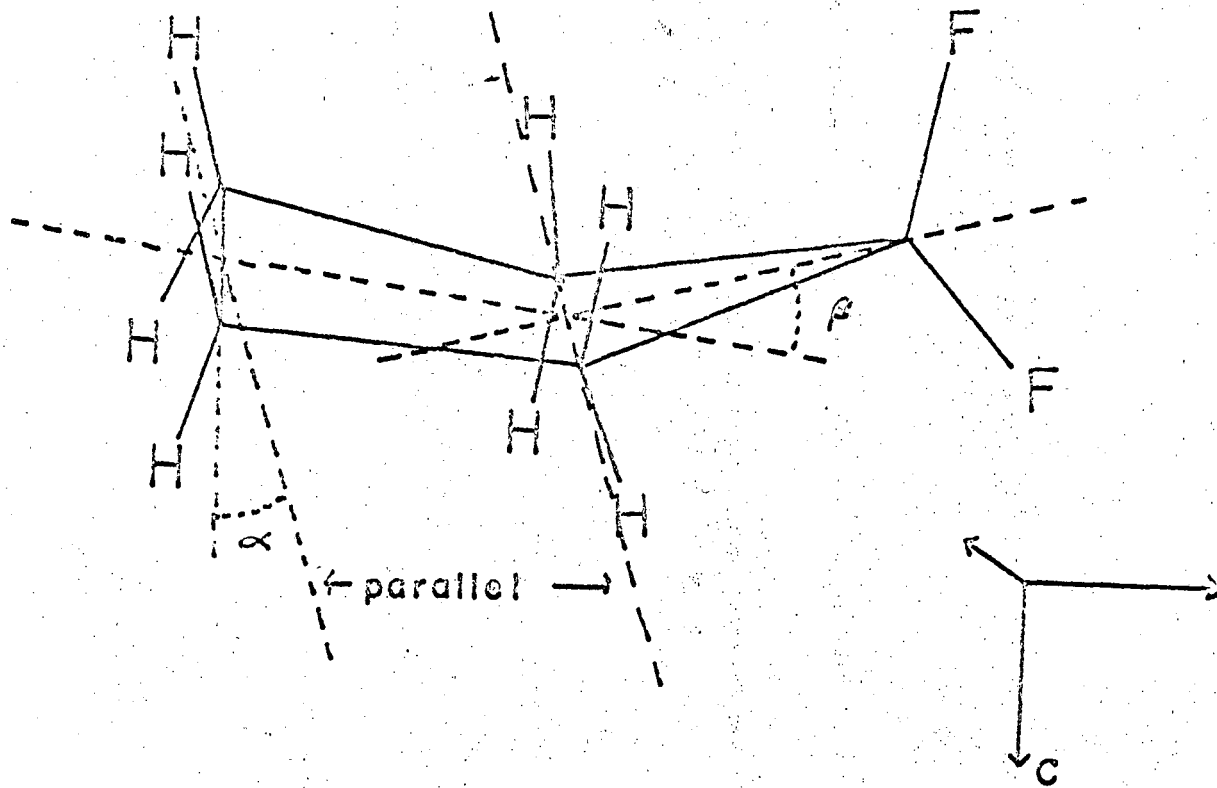
XBL 6811-6171

Fig. I-5

Fig. I-6



NBL 6811-6170



All	C—C	1.54 Å	∠ HCH	111°
All	C—H	1.09 Å	∠ FCF	108°
All	C—F	1.34 Å		

Fig. I-7

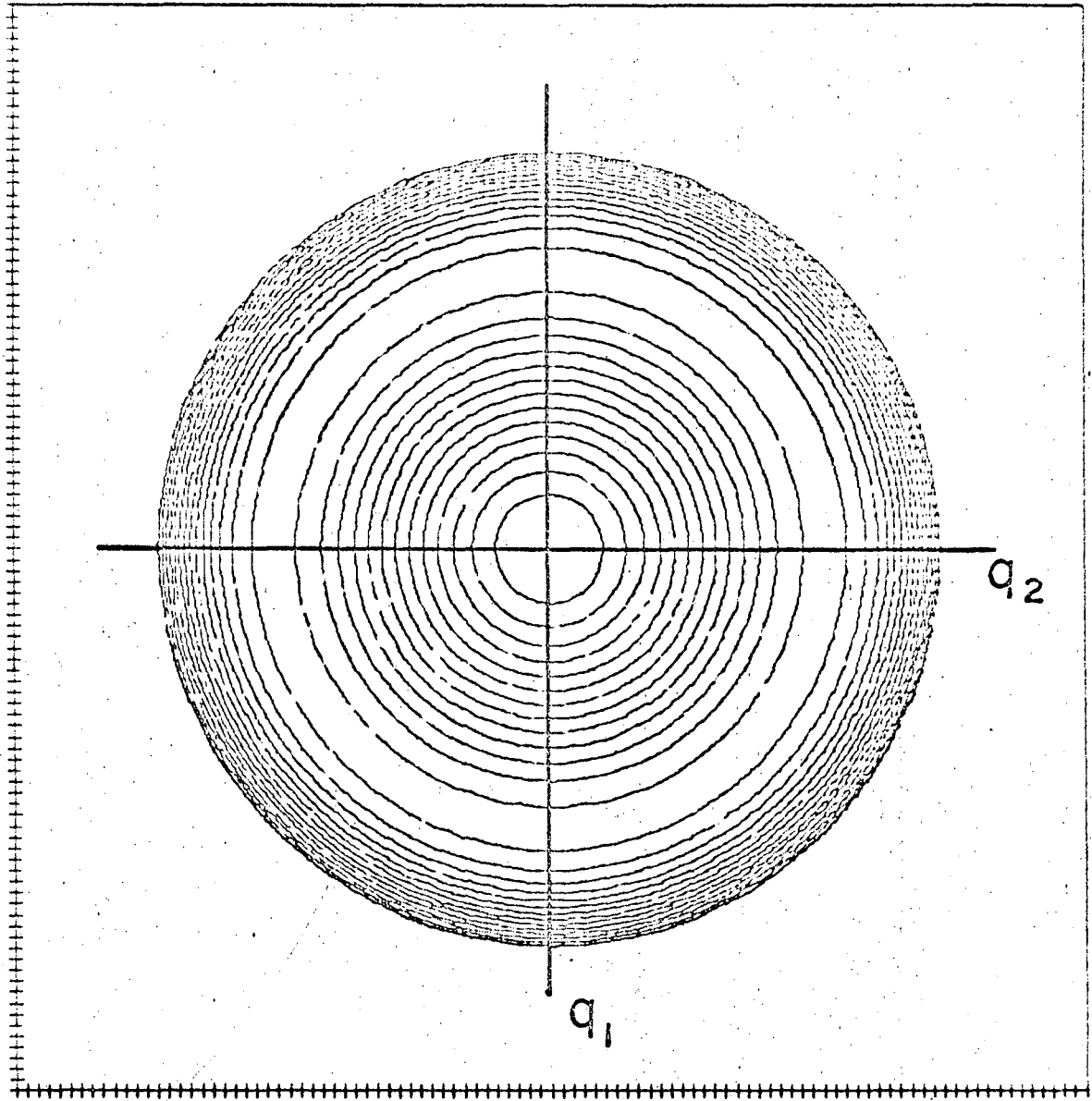


Fig. I-8(a)

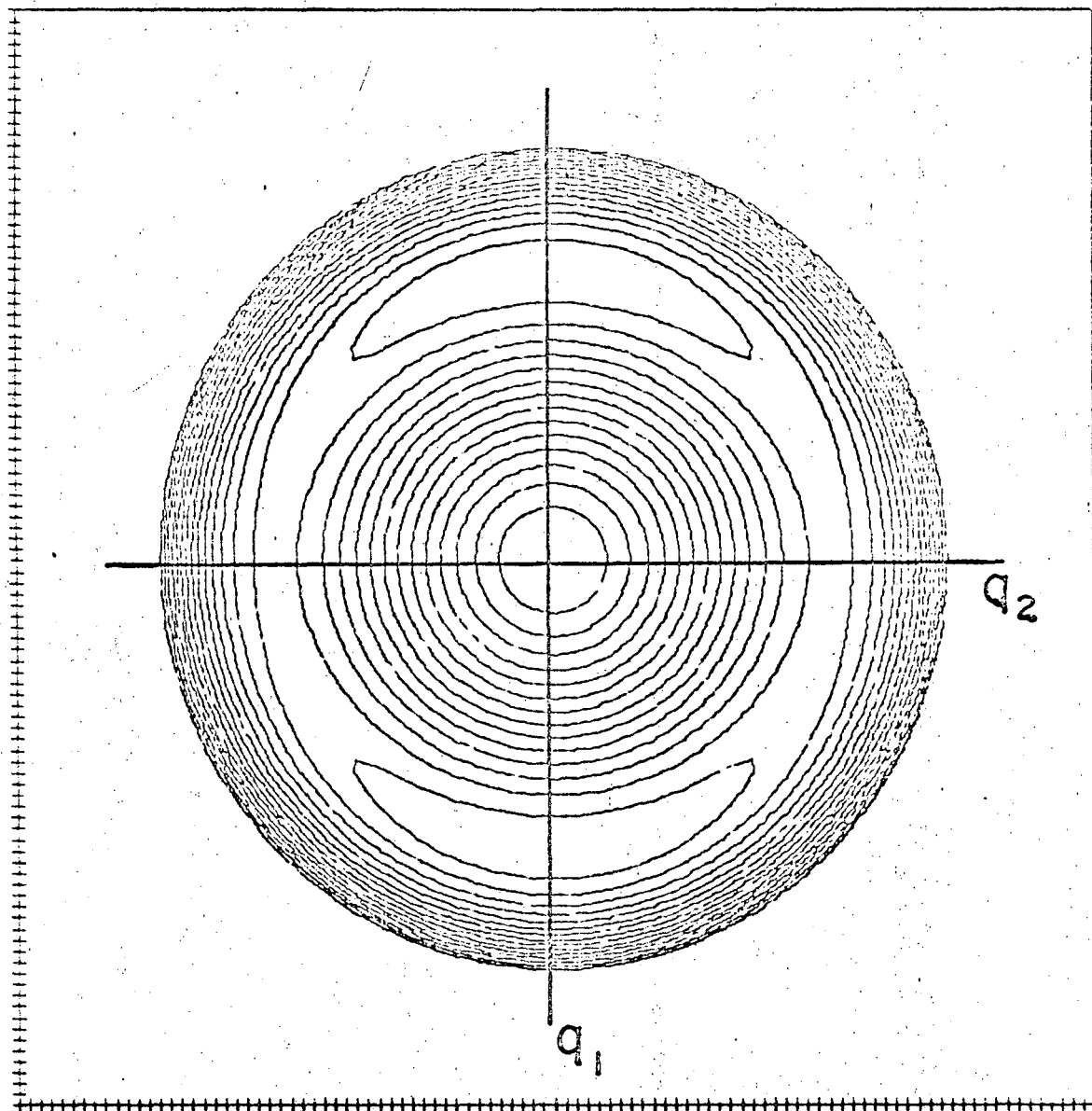


Fig. I-8(b)

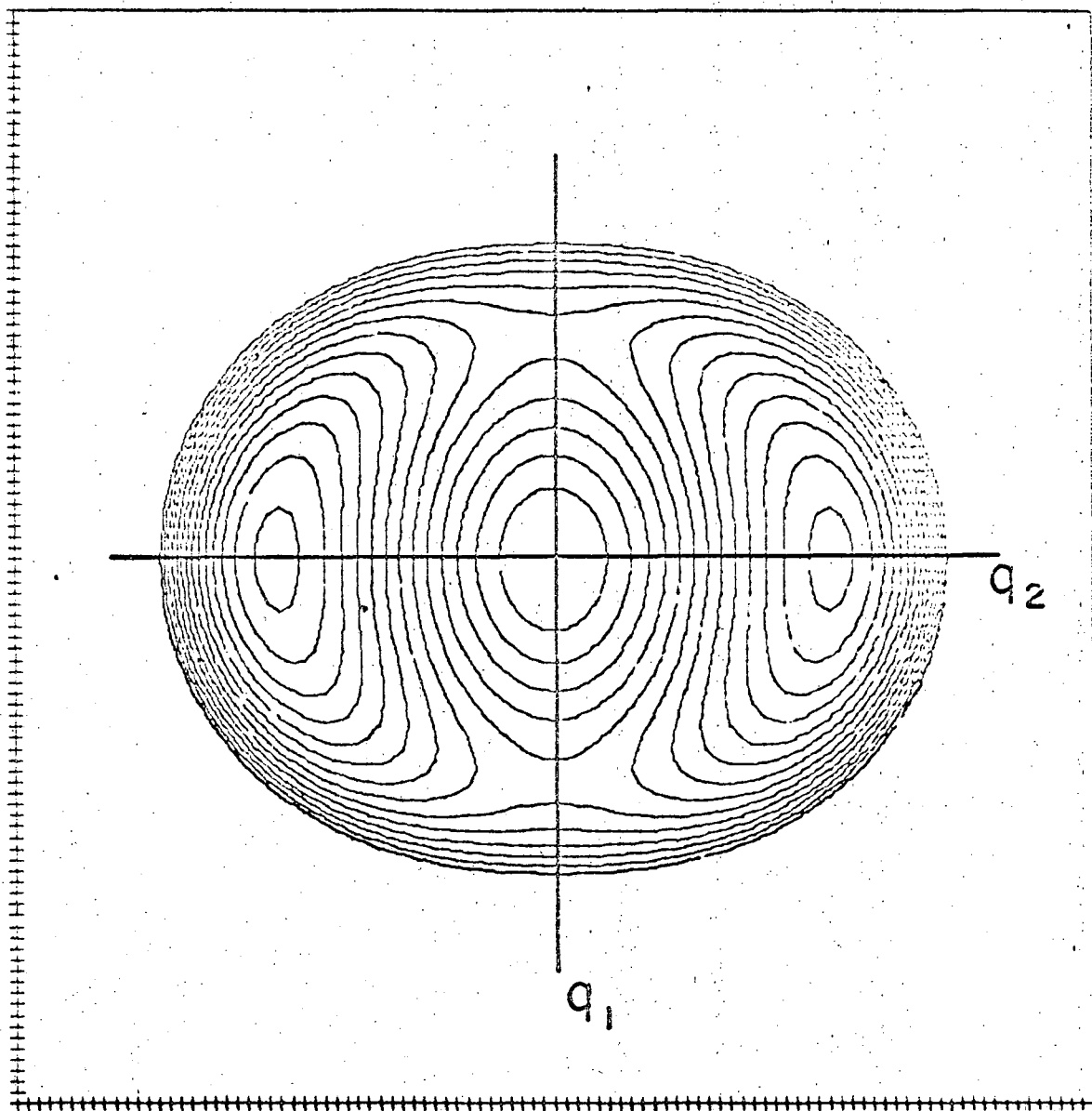


Fig. I-8(c)

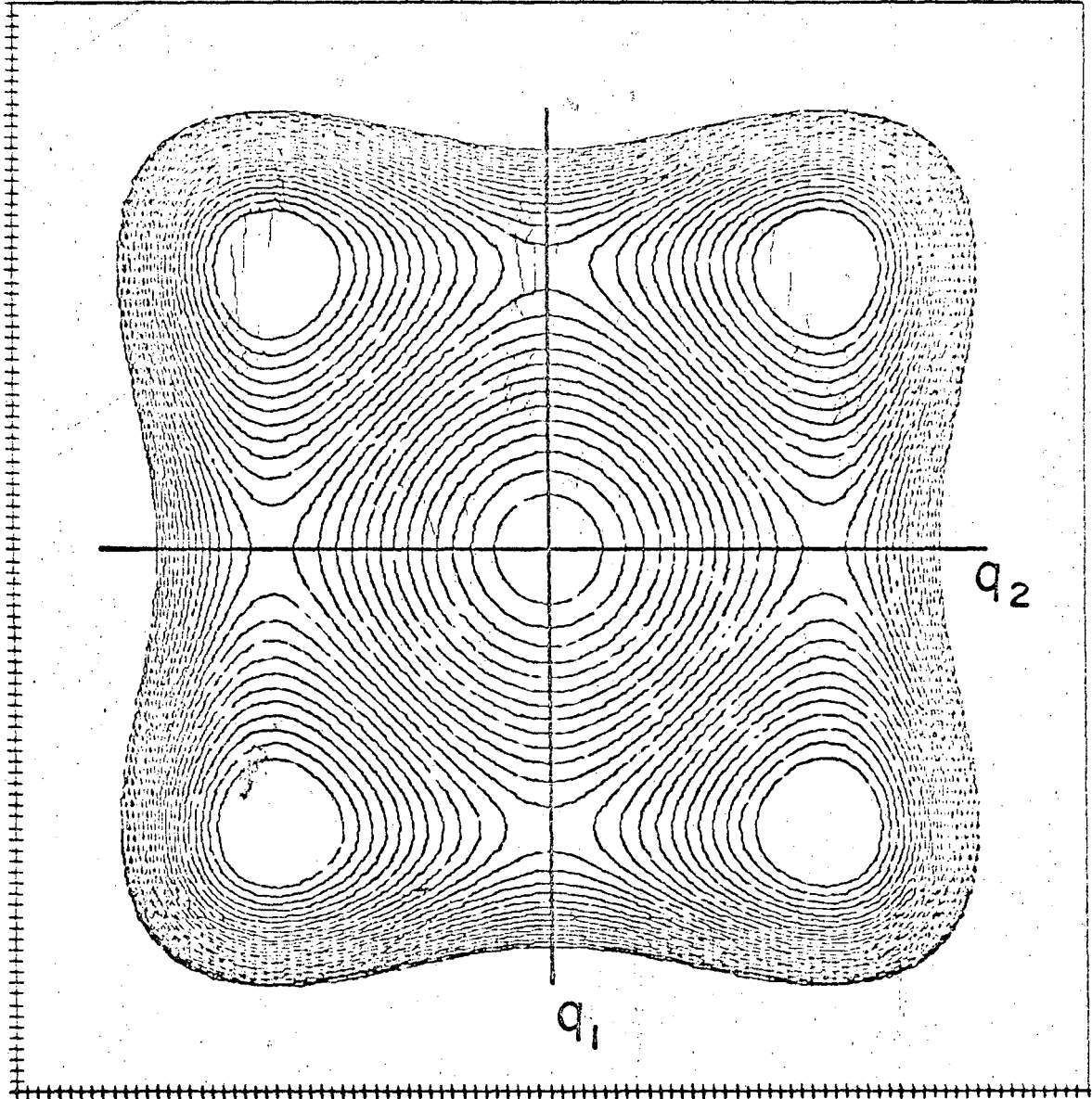


Fig. I-8(d)

THE CYCLOPENTANE SYMMETRIES

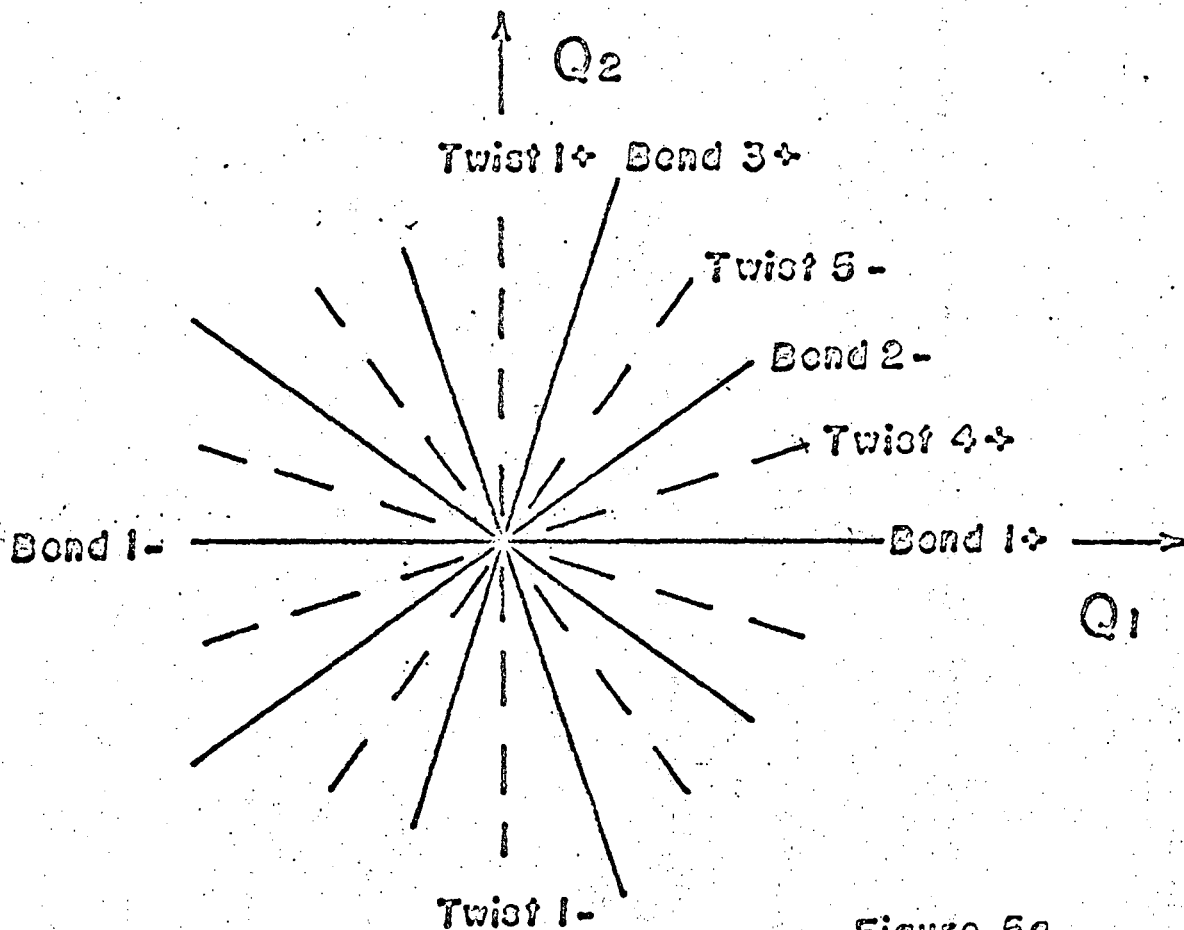


Figure 5a

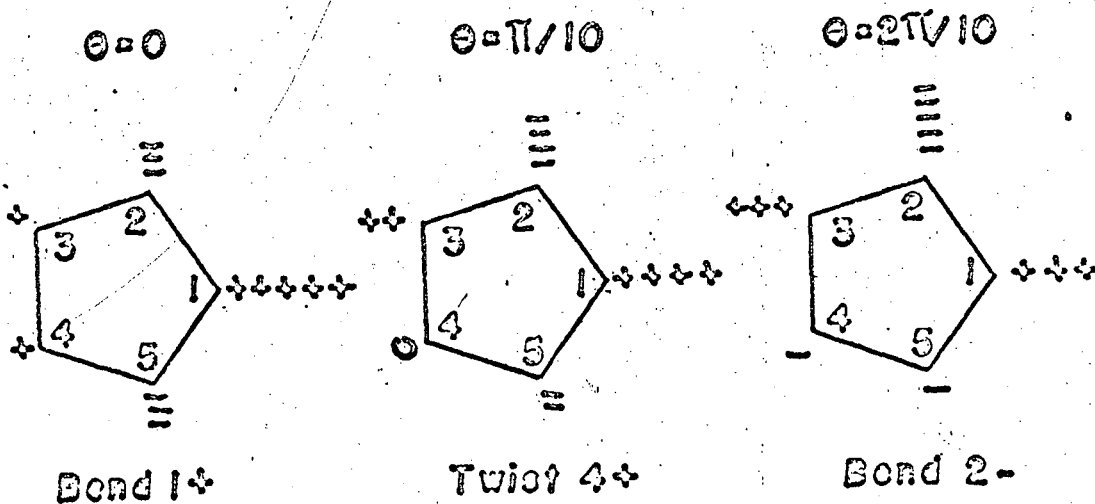


Fig. I-9

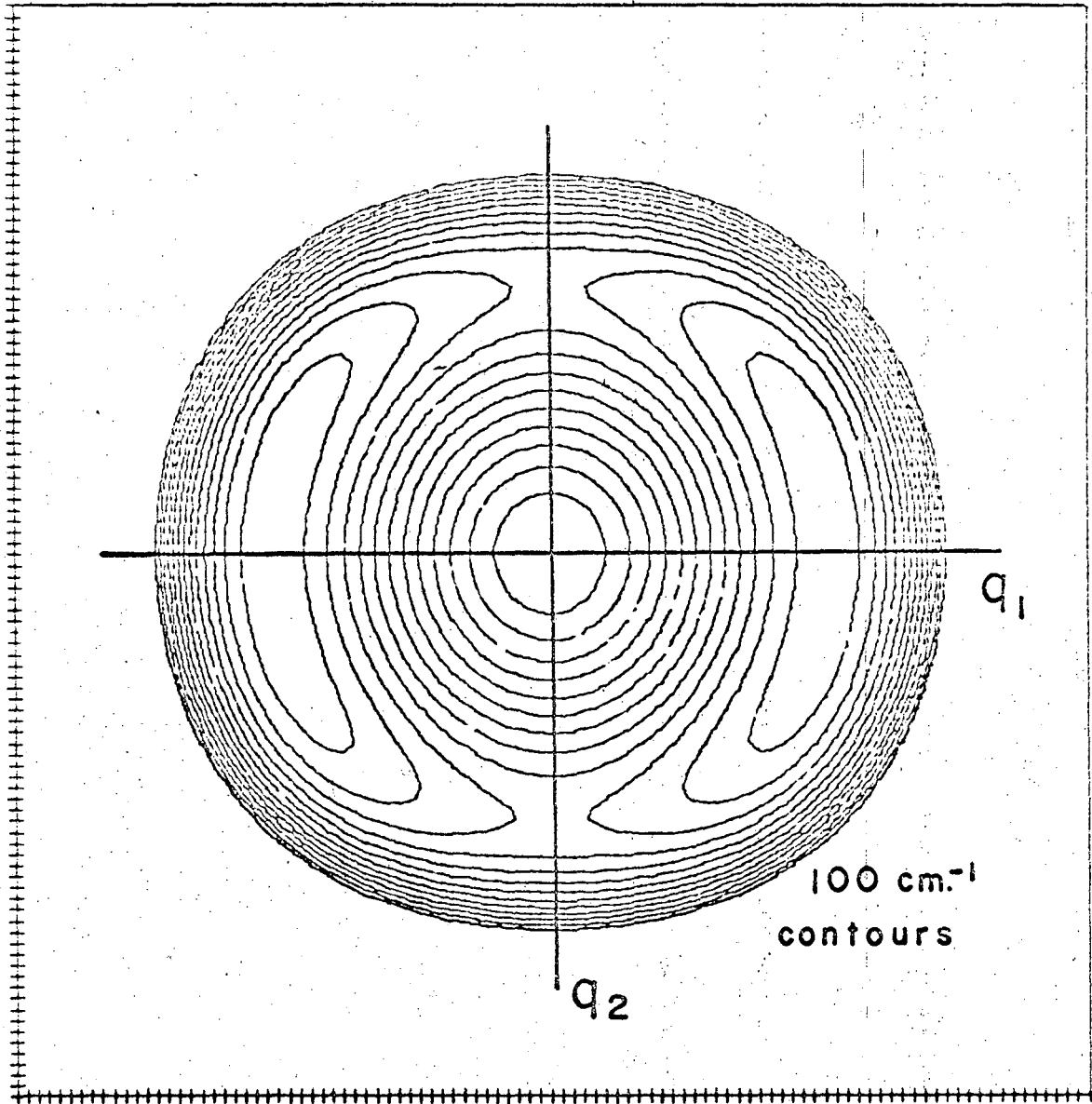


Fig. I-10

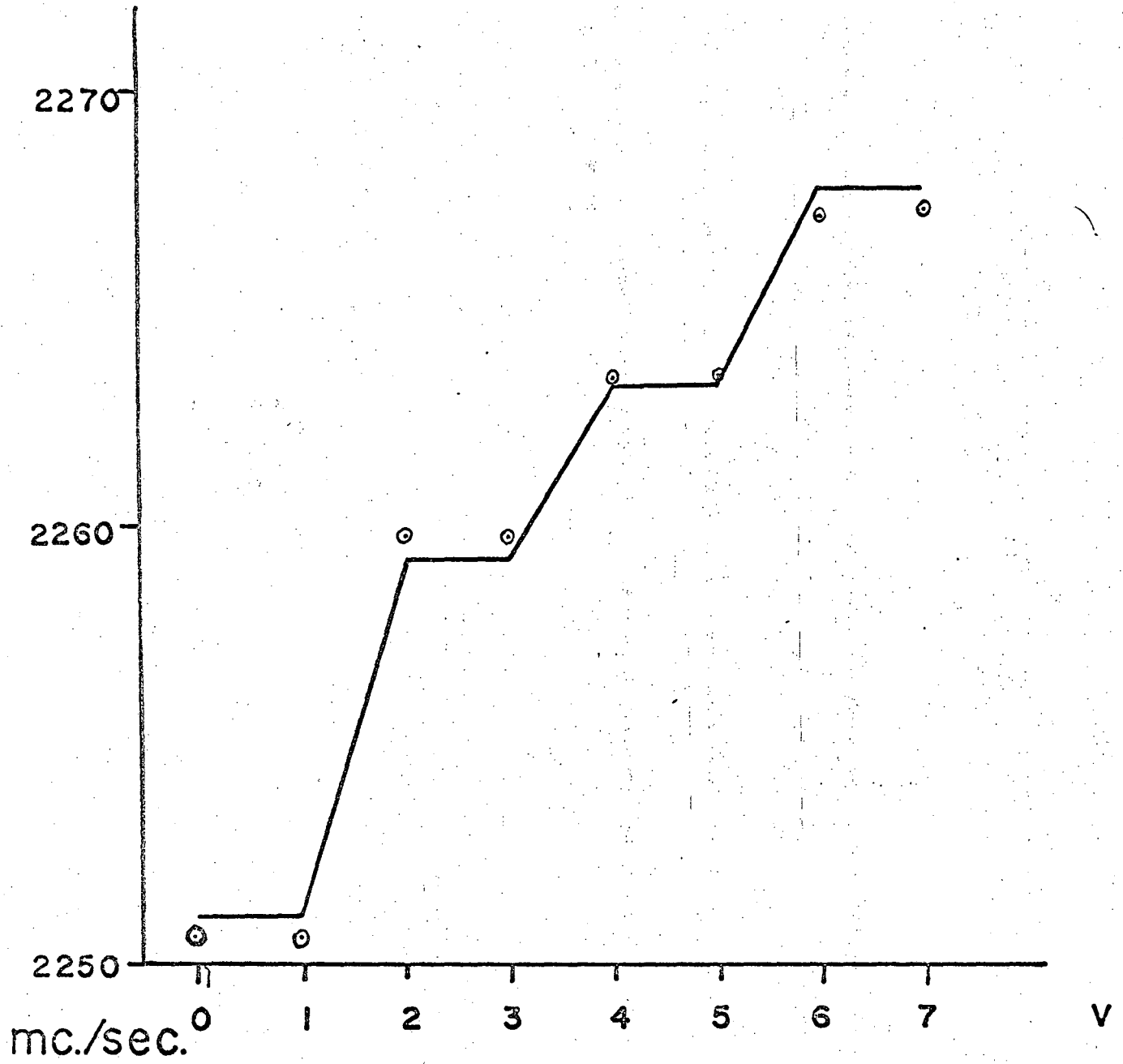


Fig. I-11

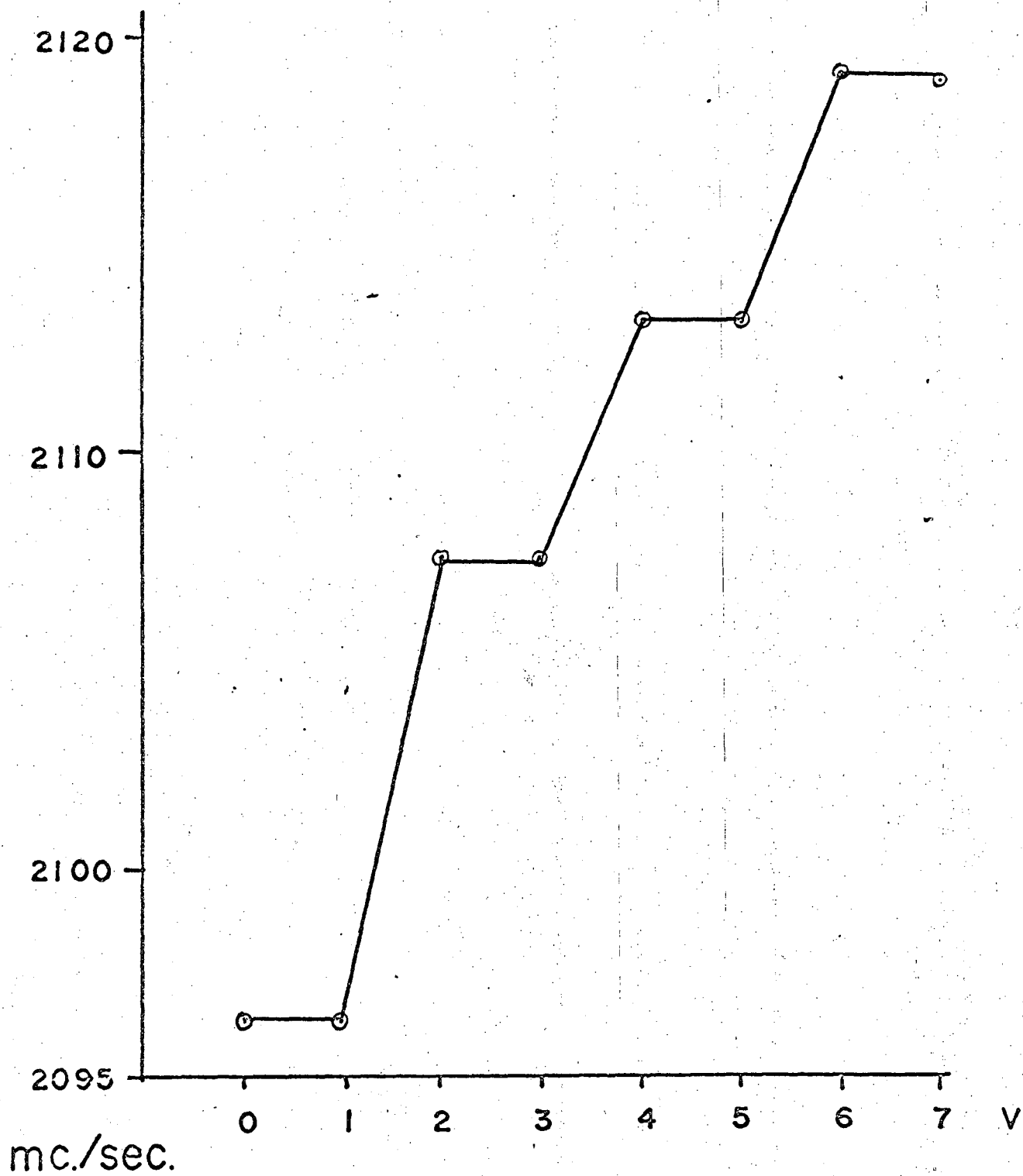


Fig. I-12

PART II

COMPUTERS AS INTERACTIVE DEVICES IN
CHEMICAL EXPERIMENTS

Over the past several years there has been a tremendous increase in the use of digital computers in chemical experiments as direct interactive devices. Today the availability of small low-cost computers has allowed such experiments to become almost commonplace.

In 1963, shortly after the original paper on digital time-averaging of magnetic resonance signals by Klein and Barton,¹ the Chemistry Department of the University of California purchased a small-to-medium sized digital computer primarily to stimulate interest in these types of experiments. Since that time a large number of experiments have been connected "on line" to this computer. This author effected the first, very simple, interface, with an NMR spectrometer, and was involved less directly in a much more complex connection with a microwave spectrometer. This section discusses briefly the former interface (the latter is described in detail in ref. 2) and also treats in a general sort of way some of the advantages of a computer-coupled experiment system and the differences between various types of systems.

Before describing the NMR experiment it would be well to mention the general goals of computer experiments and the particular goals of our experiment. The first and most obvious reason for the construction of any computer-coupled system is for time averaging. In conventional systems filtering is most easily done electronically. If the machine noise is "white" or completely random, time constant filtering allows a signal to noise ration (S/N) increase proportional to $t^{1/2}$ where t is the time spent on the experiment. Almost all actual physical chemistry experiments are limited by noise which has a $1/f$ (f is the "frequency" of the noise) component which becomes increasingly important as longer

time constants are used. Under these conditions it is easily seen that increasing the time spent on an experiment above a certain limit will be to no avail in improving S/N. If filtering is done by digital averaging of a large number of sweeps, however, it is seen that $S/N \propto n^{1/2}$ where n is the number of sweeps regardless of the characteristics of the noise spectrum. Since for constant sweep speed $t \propto n$, $S/N \propto t^{1/2}$. Time averaging will never give inferior results to electrical averaging by a time constant, and is a considerable improvement for low frequency noise reduction. We would like to know how much improvement time averaging may yield practically. For many chemical experiments, the $1/f$ component of the noise becomes appreciable at \sim l cps. Under these conditions and for reasonable averaging times, we may expect an improvement of S/N of a factor of 10 or 20, but little more. In experiments on transient phenomena which must be carried out very rapidly, repetition of the experiment many thousands of times may give S/N increases of greater than 100.

There are a number of other advantages to digitization of data. Savitsky³ has discussed several techniques of treating data when it is in digital form so as to bring to light facts which are implied by the raw data, but which may not be immediately obvious. Curve smoothing by fitting data to a simple polynomial allows for increased S/N at the expense of resolution. Since this type of filtering is done in the frequency, rather than the time, domain, many trials may be made on a high-speed computer without wasting instrument time. Conversely, resolution may be enhanced by convolution techniques in which, typically, the second derivative of the data is added to the raw data with the appropriate weighting factor. If, as is often the case, the shape of an absorption

line is known, the data may be directly fitted to this shape function, or or a sum of several, to yield the spectral parameters of interest. To do this it is necessary to have the data in digital form. Lusebrink⁴ has shown that the shape function need not be expressed as a mathematical function, but may instead be just a set of data points. There are still other advantages of digitized data. It may be readily sorted on magnetic tape and recalled at some future time. Thus a time-averaging experiment could be started at one time and completed at a much later date.

To this point we have not discussed the computer as a controller of experiments. This is where a full scale digital computer has a tremendous advantage over the simple pulse-height analysers used for the first NMR time averaging experiments. The computer and the various experiments which are on-line may form a truly interactive system. An instruction from any given experiment may generate a chain of events in the computer, which in turn may give instructions to that experiment, or, it desired, any other one. The mechanism of these instructions is discussed in ref. 2 and will not be discussed here. They may take many different forms. For instance computer instructions might be "change oscillator to new frequency xxx", or "step motor A one step clockwise", or "ring bell indicating computer error". Instructions to the computer might be: "read voltage A and store" or "stop sweeping and return data on D/A convertor".

In time averaging experiments it is particularly useful to have the computer in the central loop as there may otherwise be difficulties in adding successive sweeps with absolute registration of frequencies. It is, of course, possible to read both a frequency and a voltage, but this approach requires that there be many channels over a line-width in order

that the data not be distorted. If the computer is used to control the frequency (I have assumed the abscissa co-ordinate to be "frequency" throughout, but it may just as well be "magnetic field", "distance", "mass number", or some other coordinate depending on the experiment) this problem is eliminated.

A. THE NMR EXPERIMENT

In connecting the first experiment to our computer, our aim was to achieve useful results without spending a great deal of time on the establishment of an elaborate system. In addition we were less interested at first in S/N improvement by time-averaging than in just obtaining data in the digital form necessary for various types of "curve decomposition" routines.¹¹ For these reasons the system used did not attempt to use the computer in the control loop as described in the last paragraph.

A block diagram of the system is shown in Fig. 1. The normal mechanical sweep of the Varian A-60 spectrometer was used. Moveable micro-switches were placed to limit the motion of the carriage of the recorder, and thereby the magnetic field, to the region of interest. Data were taken only while sweeping in one direction; the rapid sweep motor was used to return the carriage for another sweep.

Data were taken on a time base provided by a variable oscillator, C. This was gated with a signal EOF which reflected whether the spectrometer was in a "sweep" or "return" configuration, and with a signal ER which became true only in case the computer did not respond to a request to accept data within one half-cycle of C. The rest of the circuitry is used to detect such an error and to reset the spectrometer to the start of a new sweep if an error were encountered.

There was found to be one primary difficulty with this system which was the lack of absolute channel registration, i.e. there are no conditions to insure that one sweep adds exactly on top of the previous ones. One method used to minimize this problem was to search each sweep to find the position of the maximum of the first line and to insure that this point at least would add coherently by shifting the abscissa of the spectrum the necessary amount. This procedure would have proved satisfactory were there not small variations in sweep rate as well as drifts in the magnetic field control loop of the spectrometer (the A-60 uses an external standard for control). The drifts were small and only of importance when trying for maximum resolution over a relatively long sweep. In some experiments each sweep was scaled so as to allow two points of the spectrum to add coherently. This reduced the problem still further, but never completely eliminated it.

Figure 2 shows the results of a time averaging experiment. The sample was an organic unknown in a micro-cell. The time average spectrum shows a number of features that previously were completely buried in the noise.

B. GENERAL CONSIDERATIONS

Our experience both with the NMR experiment and the more complex microwave one in which the computer controls directly the microwave spectrometer, was with a moderately large centralized data acquisition system. A block diagram of the system is shown in Fig. 4. An alternative approach is for each experiment to form its own small interactive system. In its simplest form each experiment would have an A/D converter and a digital tape unit or paper tape punch. The data could then be treated at a later time on a large computer. This approach has one

striking advantage over the large system: it is easily and quickly constructed and is simple enough so that difficulties with hardware are not likely to occur. There are, however, a number of considerations which, taken together, may make instead a system similar to that of the Berkeley Chemistry Department very attractive. The first is cost. Even a relatively slow low-cost computer is capable of handling a large number of experiments simultaneously. If each of these experiments were to have separate converters the cost might be greater than for the large system. The second, as previously discussed, is the capability of using the computer as a controlling and not just a data acquisition device. Along with its other advantages this aspect of the large system may save operator time. There are other advantages of the centralized system. Computation may be done on the data simultaneous with acquisition. In a time-averaging experiment, the summed data may be continually displayed in some convenient form, allowing the researcher to use only as much time as necessary to achieve the desired S/N. In conclusion we feel that when it is desired to digitize the data from a large number of experiments for purposes of time averaging, curve decomposition etc., a centralized time-shared system may well be more advantageous than individual digitizing systems.

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4. T. R. Lusebrink, Ph.D. Dissertation, University of California (1965).

PART II - FIGURE CAPTIONS

- Fig. II-1 NMR-Computer interface
- Fig. II-2 Time averaged NMR spectrum of organic unknown
- Fig. II-3 Computer system

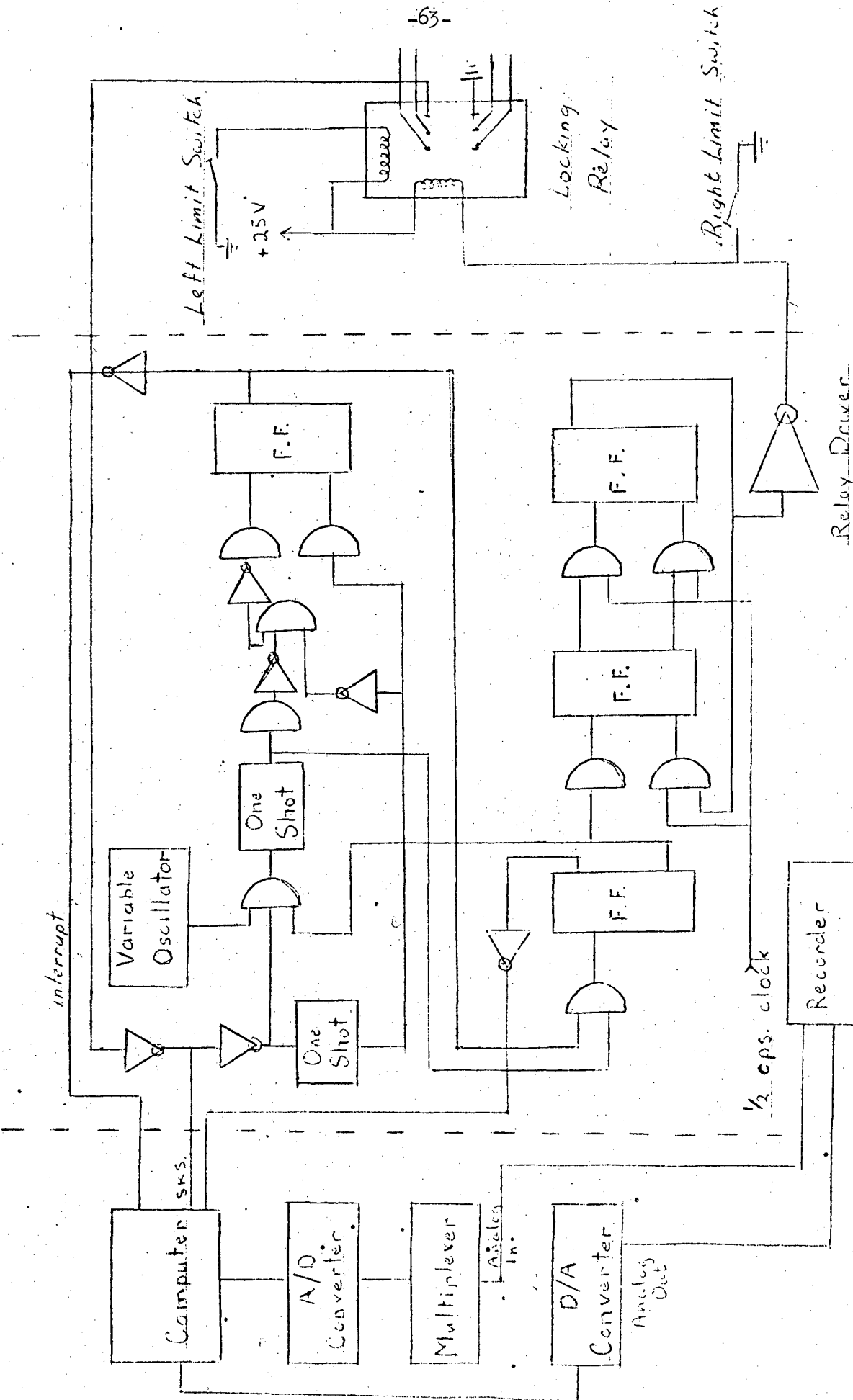


Fig. II-1

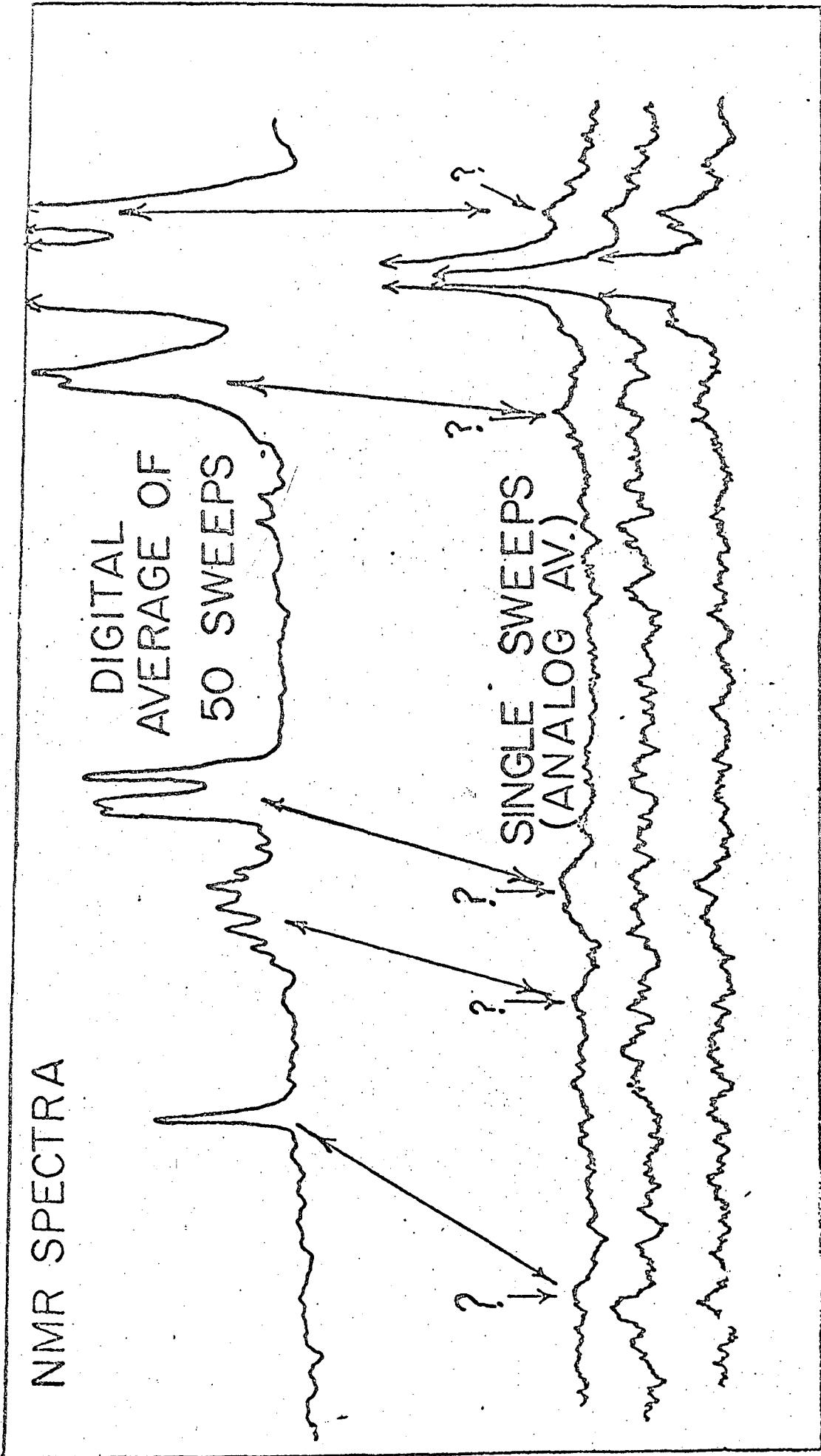
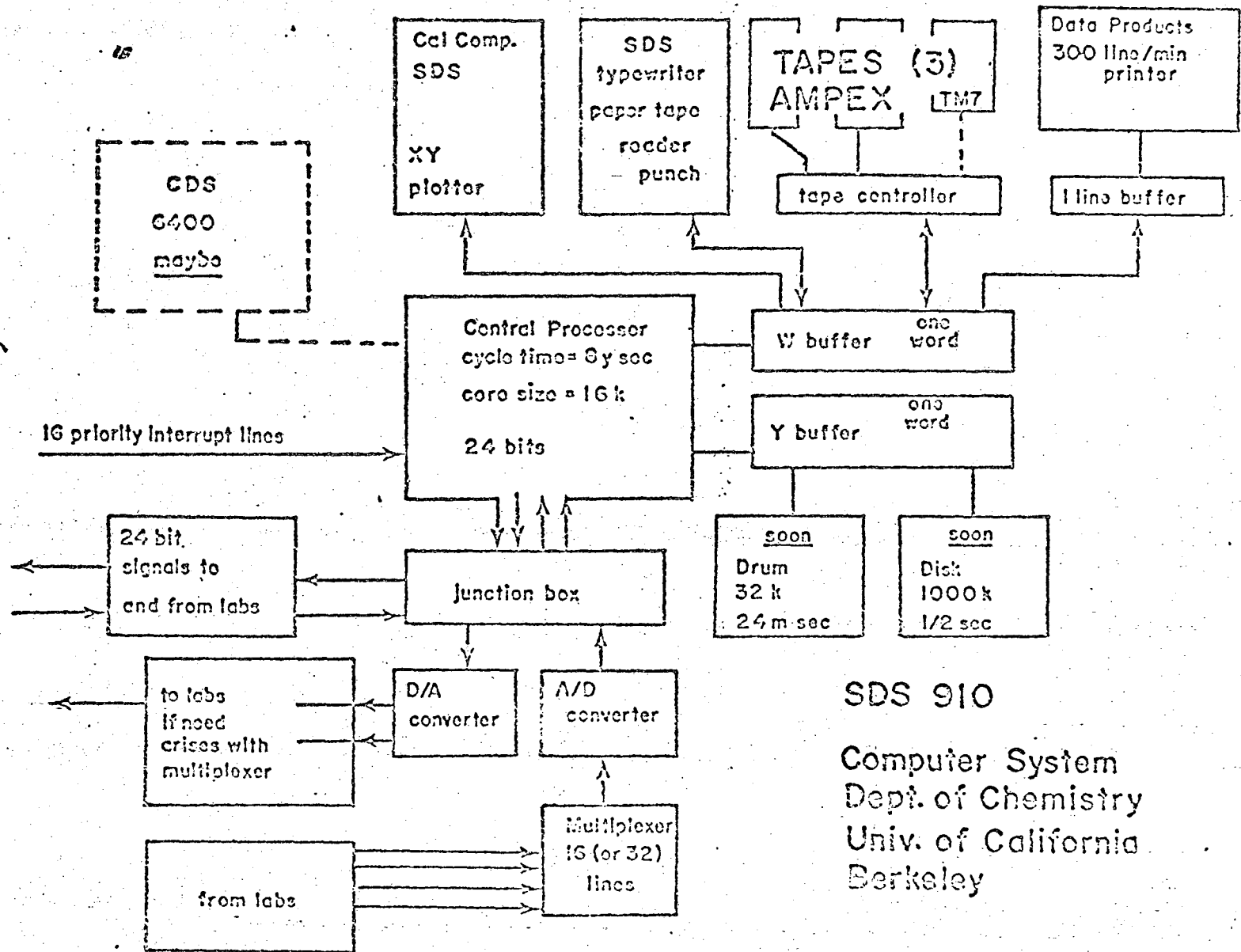


Fig. III-2

FIG. II-3



SDS 910
Computer System
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Univ. of California
Berkeley

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