Microwave Determination of the Centrifugal Distortion Constants of CH₃Cl, CH₃Br, CH₃I, BrCN, and ICN*

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The values of B, D_J , and D_{JK} in the ground vibrational state for the heavier methyl halides, and values of B and D_J for BrCN and ICN have been calculated from microwave spectroscopic measurements in the three to five-mm wave-length region. The values of B_0 in Mc/sec., D_J in kc/sec., and D_{JK} in kc/sec. in that order are, for CH₃Cl³⁶: 13292.95, 26.4, and 189; for CH₃Cl³⁷: 13088.24, 27.0, and 184; for CH₃Br⁷⁹: 9568.188, 11.1, and 129.4; for CH₃Br⁸¹: 9531.845, 10.7, and 129.0; for CH₃I: 7501.310, 7.95, and 99.4. Values of B_0 in Mc/sec. and of D_J in kc/sec. are, for Br⁷⁹CN: 4120.230 and 0.91; for Br⁸¹CN: 4096.804 and 0.81; for ICN: 3225.578 and 0.88. Frequencies of observed lines are given in tables for calibration purposes.

I. INTRODUCTION

I N order to obtain additional information concerning the chemical bonds existing in the methyl halides and in the cyanogen halides, the rotational spectra of the above-named molecules have been measured in the three to five-mm wave-length region. A secondary purpose was to establish some standard frequencies for calibration purposes in this region. The results of this investigation have been combined with information gained from other J-transitions already reported¹ to determine the values of B, D_J , and D_{JK} in the expression for the frequency of a given J transition for a non-

TABLE I. The hyperfine structure of the rotational transition $J=2\rightarrow 3$ for CH₃Cl³⁵.

F Transition	v(observed) (Mc/sec.)	v(calculated) ^a (Mc/sec.)	Calculated relative intensity						
	K=0								
$7/2 \rightarrow 9/2$ $5/2 \rightarrow 7/2$	79755.68±0.16	79755.74	100*						
$3/2 \rightarrow 5/2$ $1/2 \rightarrow 3/2$	79751.02	79751.09	52**						
$7/2 \rightarrow 7/2$ $5/2 \rightarrow 5/2$ $3/2 \rightarrow 3/2$	79736.96 79764.56 79769.94	79736.96 79764.51 79769.87	17† 4 3						
		K = 1							
7/2→9/2 5/2→7/2	79755.68 79751.02	79755.73 {79751.04}	Included in * above Included in ** above						
$3/2 \rightarrow 5/2$ $1/2 \rightarrow 3/2$	79755.68	(79750.90) 79755.60	Included in * above						
		K = 2							
$7/2 \rightarrow 9/2$ $5/2 \rightarrow 7/2$ $1/2 \rightarrow 3/2$ $7/2 \rightarrow 7/2$ $5/2 \rightarrow 5/2$	79755.68 79736.96 79768.98 79755.68 79736.96	79755.68 79736.89 79769.09 79755.68 79736.89	Included in * above Included in † above 5 Included in * above Included in † above						

• Calculated using the constants given in Table III. Second-order effects are negligible here.

¹ See individual tables for references.

rigid symmetric-top molecule:²

$$\nu_r = 2B(J+1) - 4D_J(J+1)^3 - 2D_{JK}(J+1)K^2 \quad (1)$$

which, for a linear molecule, reduces to:

$$\nu_r = 2B(J+1) - 4D_J(J+1)^3. \tag{2}$$

II. APPARATUS

The absorption cell consisted of a section of coin silver K-band wave guide approximately seven feet long into which energy was introduced at either the second or third harmonic of the reflex klystron oscillator tube fundamental using multipliers of a type already described.³ The single-crystal detection system was employed. Frequencies were measured at the oscillator tube fundamental by means of a secondary frequency

the second s			
F Transition	v(observed) (Mc/sec.)	v(calculated) (Mc/sec.)	Calculated relative intensity
		K = 0	
$7/2 \rightarrow 9/2$ $5/2 \rightarrow 7/2$	78527.10 ± 0.16	78527.22	100*
$3/2 \rightarrow 5/2$	78523.32	78523.56	61**
$7/2 \rightarrow 7/2$	78512.80	78512.46	4
		K = 1	
7/2→9/2	78527.10	78527.00	Included in * above
$5/2 \rightarrow 7/2$	78523.32	$\{78523.31\\78523.21\}$	Included in ** above
$1/2 \rightarrow 3/2$	78527.10	78526.90	Included in * above
		K=2	
7/2→9/2	78526.14	78526.32	22†
$5/2 \rightarrow 7/2$	78511.68	78511.56	16†† 11¶
$3/2 \rightarrow 3/2$	78522.00	78526.32	II I Included in t above
$5/2 \rightarrow 5/2$	78511.68	78511.56	Included in the above
$3/2 \rightarrow 3/2$	78522.00	78522.10	Included in ¶ above

TABLE II. The hyperfine structure of the rotational transition $J=2\rightarrow 3$ for CH₃Cl³⁷.

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^{*} Calculated using the constants given in Table III. Second-order effects are negligible here.

²G. Herzberg, Infra-Red and Raman Spectra of Polyatomic Molecules (D. Van Nostrand Company, Inc., New York, 1945), p. 31. See also reference 7

p. 31. See also reference 7. ³ Smith, Gordy, Simmons, and Smith, Phys. Rev. 75, 260 (1949).

TABLE III. Frequencies of hypothetical unsplit rotational lines, ν_0 , and resulting molecular constants for methyl chloride from the rotational transitions $J=0\rightarrow 1$ and $J=2\rightarrow 3$.

K	ν ₀ (Mc/sec.)	Bo (Mc/sec.)	D_J (kc/sec.)	DJK (kc/sec.)	<i>I_B</i> (10 ⁻⁴⁰ g cm ²)				
	CH ₃ Cl ³⁵								
	$J = 0 \rightarrow 1$		•						
0	26585.77ª								
	$J = 2 \rightarrow 3$	13292.95 ± 0.01	26.4 ± 0.3	189 ± 1	63.10 ₉₀ ^b				
0	79754.85								
1	79753.75								
2	79750.30		0107						
		CH	.3Cl ³⁷						
	$J=0\rightarrow 1$								
0	26176.37ª								
	$J = 2 \rightarrow 3$	13088.24 ± 0.02	27.0 ± 0.4	184 ± 2	64.09 ₆₁ ^b				
0	78526.51								
1	78525.47								
2	78522.05								

TABLE IV.—Continued.

F	ν(observed)	v(calculated)	Calculated relative intensity
Transition	(Mc/sec.)	(Mc/sec.)	
		K=3	
9/2→11/2	76207.66	76207.88	43
3/2→5/2	76152.28	76152.54	18

* Calculated using the constants given in Table VI. Second-order effects are also included here. ^b This value includes the intensity of the line for $F = 5/2 \rightarrow 7/2$, K = 3, since this line was not resolved at the pressures used.

TABLE V. They hyperfine structure of the rotational transition $J=4 \rightarrow 5$ for CH₃Br.

	F Transition	v(observed) (Mc/sec.)	v(calculated) ^a (Mc/sec.)	Calculated relative intensity
184 ± 2 64.09_{61}		C	H_3Br^{79}	
	$11/2 \rightarrow 13/2$ $9/2 \rightarrow 11/2$	95673.51±0.27	$\begin{cases} 95673.33 \\ 95673.32 \end{cases}$	57
243 (1948). J. W. M. DuMond and	$7/2 \rightarrow 9/2$ $5/2 \rightarrow 7/2$	95683.62	{95683.16 {95683.19}	100*
			K=1	
of the rotational H ₃ Br.	$11/2 \rightarrow 13/2$ 9/2 $\rightarrow 11/2$ 7/2 $\rightarrow 9/2$	95669.97 95677.20 95683.62	95669.71 95676.90 95683.26	30 25 Included in * above
 Calculated relative intensity 	5/2→7/2	95676.39	95676.04	16
	11/2 12/2	05650 20	K = 2	26
	$9/2 \rightarrow 11/2$	95688.27	95687.65	20 21
67	$7/2 \rightarrow 9/2$ $5/2 \rightarrow 7/2$	95683.62 95654.73	95683.55 95654.58	Included in * above 14
100*			K=3	
	11/2→13/2	95640.87	95640.80	40
	9/2→11/2	95706.12	95705.65	33
36 27	7/2→9/2 5/2→7/2	95683.62 95619.24	95683.98 95618.95	Included in * above 21
15			K = 4	
	11/2→13/2	95615.73	95615.48	11
29		С	H ₃ Br ⁸¹	
22 Included in * above			K=0	
12	$11/2 \rightarrow 13/2$ 9/2 $\rightarrow 11/2$	95310.78	<pre>{95310.58 95310.58</pre>	57
43	$7/2 \rightarrow 9/2$ $5/2 \rightarrow 7/2$	95319.12	{95318.81 {95318.83}	100**b
33 Included in * above			<i>K</i> =1	
18	$11/2 \rightarrow 13/2$	95307.48	95307.35	30
	7/2→9/2	95319.12	95318.68	Included in ** above
			K=2	
67	$11/2 \rightarrow 13/2$	95297.55	95297.68	26
	$9/2 \rightarrow 11/2$	95322.15	95321.73	21
} 100*b	5/2→1/2	93233.89	95294.12	14
	44 10 42 10	05004 53	K=3	40
36	$11/2 \rightarrow 13/2$ 0/2 $\rightarrow 11/2$	95281.53	95281.54	40
27	$5/2 \rightarrow 7/2$	95263.47	95263.29	21
Included in * above 15			K = 4	
	11/2→13/2	95259.24	95258.92	11
29				
22 Included in * above	Calculated are also include	using the constants d here.	s given in Table	VI. Second-order effects

^a Gordy, Simmons, and Smith, Phys. Rev. **74**, ^b Using $h = 6.62373 \times 10^{-27}$ erg sec. as given by E. R. Cohen, Rev. Mod. Phys. **21**, 651 (1949).

TABLE IV. The hyperfine structure of transition $J=3\rightarrow 4$ for CF

F Transition	ν (observed) (Mc/sec.)	ν(calculated) ^a (Mc/sec.)	Calculated relative intensity	
	C	H ₃ Br ⁷⁹		1
	i	K=0		1
$\begin{array}{c} 9/2 \rightarrow 11/2 \\ 7/2 \rightarrow 9/2 \end{array}$	76538.02 ± 0.18	$\left\{\begin{matrix} 76538.31 \\ 76538.30 \end{matrix}\right\}$	67	
$3/2 \rightarrow 7/2$ $3/2 \rightarrow 5/2$	76554.82	{765554.96 {76555.03}	100*	
	i	K = 1		1
$9/2 \rightarrow 11/2$ 7/2 $\rightarrow 9/2$ 5/2 $\rightarrow 7/2$	76532.88 76547.24 76554.82	76533.13 76547.49 76555.00	36 27 Included in * above	
3/2→5/2	76540.20	76540.52	15	
	i	K = 2		1
9/2→11/2 7/2→9/2	76517.36 76575.22	76517.59 76575.18	29 22	
$5/2 \rightarrow 7/2$ $3/2 \rightarrow 5/2$	76554.82 76496.60	76555.07 76497.16	Included in * above 12	1
	i	K = 3		
9/2→11/2	76491.36	76491.62	43	
$7/2 \rightarrow 9/2$	76621.78	76621.59	33	
$3/2 \rightarrow 1/2$ $3/2 \rightarrow 5/2$	76554.82 76425.18	76555.09 76425.40	Included in * above 18	1
	C	H ₃ Br ⁸¹		
	Ĺ	K=0		
$\begin{array}{c}9/2 \rightarrow 11/2\\7/2 \rightarrow 9/2\\5/2 \rightarrow 7(2)\end{array}$	76248.32	{76248.39 {76248.38}	67	1
$3/2 \rightarrow 1/2$ $3/2 \rightarrow 5/2$	76261.96	76262.35	100* ^b	
,		., , K — 1		
$0/2 \rightarrow 11/2$	76243 66	76743.80	36	1
7/2→9/2	76255.68	76255.90	27	
$5/2 \rightarrow 7/2$ $3/2 \rightarrow 5/2$	76261.96 76249.94	76262.16 76250.08	Included in * above 15	
		K = 2		1
9/2→11/2	76230.18	76230.40	29	=
7/2→9/2	76278.16	76278.52	22	
$5/2 \rightarrow 7/2$ $3/2 \rightarrow 5/2$	76261.96 76213.16	76261.71 76213.36	Included in * above 12	a a

This value includes the intensities of the lines for $F = 7/2 \rightarrow 9/2$, K = 2, $F = 7/2 \rightarrow 9/2$, K = 3, since these lines were not resolved at the pressures used.

TABLE VI. Frequencies of hypothetical unsplit rotational lines, v_0 , and resulting molecular constants for methyl bromide from the rotational transitions $J=1\rightarrow 2$, $J=3\rightarrow 4$ and $J=4\rightarrow 5$.

TABLE VII. The hyperfine structure of the rotational transition $J = 4 \rightarrow 5$ for CH₃I¹²⁷.

	νο		DJ	DJK	IB (10-40	F Transition	ν(observed) (Mc/sec.)	v(calculated) (Mc/sec.)	Calculated relative intensity
	(MIC/sec.)	(MC/sec.)	(KC/Sec.)	(kc/sec.)	g cm²)		i	K = 0	
		, CH	I₃Br ⁷⁹			$13/2 \rightarrow 15/2$	75019.28 ± 0.16	75019.35	78
J	$l = 1 \rightarrow 2$					$11/2 \rightarrow 13/2$	75027.58	75027.47	63
0	38272.40ª					9/2→11/2	75004.28	75004.11	50
1	38272.04ª					7/2→9/2	74977.62	74977.65	69*
	7-2-1					$5/2 \rightarrow 7/2$	74967.66	74967.67	31
~ _	$7 = 3 \rightarrow 4$					$3/2 \rightarrow 5/2$	74986.14	74986.15	24
1	76542.43						1	r_1	
2	76538.27						1	7	.
ĩ	76533.13	$9568.188 \pm .025$	11.1 ± 0.8	129.4 ± 0.3	87.67 ₆₅ 6	$13/2 \rightarrow 15/2$	75026.20	75026.22	75
-						$11/2 \rightarrow 13/2$	75016.20	75016.11	61
j	<i>I</i> =4→5					$9/2 \rightarrow 11/2$ $7/2 \rightarrow 0/2$	74993.28	74993.30	48
0	95676.65					$\frac{1}{2} \rightarrow \frac{9}{2}$ $\frac{5}{2} \rightarrow \frac{7}{2}$	74970.22	74970.18	Jð Included in * ebeur
1	95675.36					5/2-71/2	14911.02	74977.01	included in above
2	95671.48							K = 2	
3	95664.89					$13/2 \rightarrow 15/2$	75046 48	75046 72	66
4	95655.88)				$13/2 \rightarrow 13/2$ $11/2 \rightarrow 13/2$	74082 18	74082 21	53
		CT	J D81			$9/2 \rightarrow 11/2$	74960.76	74960 75	42
	$I = 1 \rightarrow 2$)	13D1-4			$7/2 \rightarrow 9/2$	74971.76	74971.79	33
ຸ	20126.07%					$5/2 \rightarrow 7/2$	75007.62	75007.59	26
1	38120.97*								
	55120.01						1	K=3	
j.	$J = 3 \rightarrow 4$					13/2→15/2	75081.02	75080.70	100
0	76251 80					$11/2 \rightarrow 13/2$	74926.04	74926.43	81
ĭ	76250.79					7/2→9/2	74964.36	74964.51	51
2	76247.68	0521 045 1 015	107.07	120.0 1.0.2	00.01 h				
3	76242.49	(9551.845±.015	10.7 ± 0.7	129.0 ± 0.2	88.0108		1	K=4	
	7 4 F					11/2→13/2	74849.92	74849.85	23
,	/=4→5					9/2→11/2	74829.54	74829.45	18
0	95313.35								
1	95312.10					Calculated	using the constant	s given in Ta	ble VIII. Second-order
$\frac{2}{3}$	95307.90					effects are also	included here.		
4	95292.78								

• See Table III, reference a. • Using $h = 6.62373 \times 10^{-27}$ erg sec., see Table III, reference b.

standard.⁴ The absorption cell was maintained at dry ice temperature during measurements and gas pressures of about 10⁻³ mm Hg were used.

III. RESULTS

In order that some standard absorption lines for frequency comparison in the three- to five-mm wavelength region might be made available, the observed frequencies of the hyperfine structure lines for each of the *J*-transitions studied have been presented in Tables I, II, IV, V, VII, IX, and X. Frequencies falling within the range from 60,000 to 85,000 Mc/sec. were second harmonics of the klystron oscillator, those higher were the third harmonics with larger probable errors as given in the tables. No accurate measurement of relative intensities was attempted; only a general comparison of observed values with the calculated tabular values was made for line identification purposes.

Tables III, VI, VIII, and XI give the frequencies, ν_0 , of the hypothetical unsplit absorption lines for the respective molecules investigated. In every case except that of methyl chloride it was found that the second order nuclear quadrupole effects predicted by Bardeen and Townes⁵ had to be taken into account in addition to first order nuclear quadrupole interactions before satisfactory agreement between observed and calculated line positions could be obtained. The resulting molecular B_0 and centrifugal distortion constant values

TABLE VIII. Frequencies of hypothetical unsplit rotational lines, ν_0 , and resulting molecular constants for methyl iodide from the rotational transitions $J = 1 \rightarrow 2$ and $J = 4 \rightarrow 5$.

K	۷٥ (Mc/sec.)	<i>B</i> ₀ (Mc/sec.)	D_J (kc/sec.)	DJK (kc/sec.)	IB (10 ⁻⁴⁰ g cm ²)
0 1	$V = 1 \rightarrow 2$ 30004.98 ^a 30004.61 ^a				
0 1 2 3 4	$V = 4 \rightarrow 5$ 75009.15 75008.15 75005.09 75000.10 74993.30	57501.310±0.007	7.95+0.09	99.4±0.5	111.8 ₃₄ b

• See Table III, reference a. • Using value of $h = 6.62373 \times 10^{-27}$ erg sec., see Table III, reference b.

⁵ J. Bardeen and C. H. Townes, Phys. Rev. 73, 627, 1204 (1948).

⁴ R. Unterberger and W. V. Smith, Rev. Sci. Inst. 19, 580 (1948).

F Transition	v(observed) (Mc/sec.)	v(calculated)* (Mc/sec.)	Calculated relative intensity
	Br ⁷⁹ CN		
$19/2 \rightarrow 21/2$ $17/2 \rightarrow 19/2$	74162.76 ± 0.18	74162.78	${100 \\ 89}$
$15/2 \rightarrow 17/2$ $13/2 \rightarrow 15/2$	74159.48	74159.44	$\left\{\begin{array}{c} 80\\71\end{array}\right.$
	Br ⁸¹ Cn		
$19/2 \rightarrow 21/2$ $17/2 \rightarrow 19/2$	73741.20	73741.20	${100 \\ 89}$
$15/2 \rightarrow 17/2$ $13/2 \rightarrow 15/2$	73738.42	73738.41	$\left\{\begin{array}{c} 80\\71\end{array}\right.$

TABLE IX. The hyperfine structure of the rotational transition $J = 8 \rightarrow 9$ for BrCN.

^a Calculated using the constants given in Table XI. Second-order effects are also included here.

TABLE X. The hyperfine structure of the rotational transition $J = 10 \rightarrow 11$ for ICN.

F Transition	v(observed) (Mc/sec.)	ν(calculated)ª (Mc/sec.)	Calculated relative intensity
$25/2 \rightarrow 27/2$ $23/2 \rightarrow 25/2$ $21/2 \rightarrow 22/2$	70961.30 ± 0.18 70963.90 70959.14	70961.27 70963.71	100 91
$\begin{array}{c} 21/2 \rightarrow 23/2 \\ 19/2 \rightarrow 21/2 \\ 17/2 \rightarrow 19/2 \end{array}$	70959.14 b 70949.66	70959.22 70952.99 70949.79	83 76 69
15/2→17/2	b	70953.54	63

* Calculated using the constants given in Table XI. Second-order effects are also included here. ^b Observed but not measured since these lines were unresolved at the pressures used.

are shown in the same tables. In all the methyl halides the decrease in unsplit line frequency with increasing Kvalues is quite marked for each J transition. It is interesting to note that even in the case of the $J=0\rightarrow 1$ transition for methyl chloride the distortion effects are significant. Consequently, all values of B_0 are higher than those previously reported for the respective molecules. (See references accompanying the tables.) Somewhat lower values of I_B result from these, where I_B is the moment of inertia of the molecule about an axis through the center of mass perpendicular to the figure axis.

The values of line frequencies calculated using the constants for the respective molecules are given also in the tables alongside the observed frequencies and may be seen to agree rather well with these observed values.

IV. DISCUSSION

In Table XII are summarized the centrifugal distortion constants for the methyl halides. The bondstretching and bond-bending force constants calculated by Linnett⁶ for these molecules are listed there also for comparison purposes.

Since I_B for the methyl halides depends more heavily on $|\cos \angle XCH|$, where X represents the halogen, than on the sine of this angle, then the decreasing values

TABLE XI. Frequencies of hypothetical unsplit rotational lines, v_0 , and resulting molecular constants for BrCN and ICN from the rotational transitions indicated below.

J Transi- tion	ν ₀ (Mc/sec.)	Bo (Mc/sec.)	<i>Dj</i> (kc/sec.)	<i>I_B</i> (10 ⁻⁴⁰ g cm ²)
		Br ⁷⁹ CN		
$2 \rightarrow 3$ $3 \rightarrow 4$ $8 \rightarrow 9$	24721.14* 32961.79 ^b 74161.49	4120.230±0.018	0.91±0.09	203.6 ₀₆ °
		Br ⁸¹ CN		
$2 \rightarrow 3$ $3 \rightarrow 4$ $8 \rightarrow 9$	24580.56 ^a 32774.38 ^b 73740.12	4096.804±0.018	0.81±0.09	204.771
		ICN		
3→4	25804.22ª)			
4→5 10→11	32255.55 ^b 70958.06	3225.578 ± 0.018	0.88 ± 0.09	260.9 ₇₉
	-			

Townes, Holden, and Merritt, Phys. Rev. 74, 1113 (1948).
 Smith, Ring, Smith, and Gordy, Phys. Rev. 74, 370 (1948).
 Using value of h=6.62373 ×10⁻²⁷ erg sec., see Table III, reference b.

of D_J in the chloride, bromide, iodide series would indicate that $\angle XCH$ is decreasing sufficiently in the heavier compounds to offset the greater stretching of the C-X bond in these compounds which would be expected from the values of the C-X bond force constants.

The large shift in unsplit line frequencies, ν_0 , with increasing K and the positive sign for D_{JK} would indicate a considerable lengthening of the C-H bond. This is especially true since both the effect of rotation about the figure axis and the probable increase in the ionic character of the C-X bond when it stretches would lead to a decrease in \angle XCH. Values of D_{JK} which decrease for the chloride, bromide, iodide sequence would follow from the sequence of C-H bond force constants in these molecules as well as from the decreasing values of the ∠XCH bond-bending constants.

In the cases of BrCN and ICN the $C \equiv N$ bondstretching force constant should be the same in both molecules (about 17×10^5 dyne/cm) and we should then

TABLE XII. A tabulation of the centrifugal distortion constants for the methyl halides with values of corresponding bond-stretching and bond-bending force constants.

			Force constants ^a				
			C-H	C – X	x-C ^H	-c 1	
Molecule	DJ (kc/sec.)	DJK (kc/sec.)	(10 ⁵ dy	ne/cm)	(10 ⁻¹¹ dyn	H e-cm/rad)	
CH ₃ Cl ³⁵ CH ₃ Cl ³⁷	26.4 27.0	$189 \\ 184 \}$	4.90	3.35	0.701	0.523	
CH3Br ⁷⁹ CH3Br ⁸¹ CH3I	11.1 10.7 7.95	129.4 129.0 99.4	4.95 5.00	2.83 2.32	0.632 0.550	0.516 0.516	

* The values of force constants listed here are as given by Linnett (Ref. 6). Those calculated by B. L. Crawford, Jr., and S. R. Brinkley, Jr., J. Chem. Phys. 9, 69 (1941) with the assumption of a more general force field follow principally the same trend although they are somewhat different in magnitude.

⁶ J. W. Linnett, J. Chem. Phys. 8, 91 (1940).

expect the value of D_J to increase in going from BrCN to ICN due to the larger stretching of the C-X bond. The rather large limits of error prevent any definite conclusions here, although the value of D_J for ICN is larger than the average BrCN value.

It is interesting to compare the distortion constant values obtained here for the methyl halides with those calculated by Slawsky and Dennison.⁷ Using dimensions and force constants determined principally from infra-red data, they obtained values of D_J which are roughly one-tenth of the values given here. Their computed values of D_{JK} have the correct order of magni-

⁷Z. I. Slawsky and D. M. Dennison, J. Chem. Phys. 7, 509 (1939).

tude, being 1.6 to 2.5 times the experimental values, but have the opposite algebraic sign. Frequencies of the unsplit lines for K=0 computed with their values of D_J but with the I_B evaluations reported here differ by about two or three megacycles from the observed frequencies. Within the limits of experimental error, however, the variation of the line frequency shift due to centrifugal distortion expressed as a function of the values of J and K appears to be correctly predicted by Eq. (1). The authors wish to thank Dr. Walter Cordy for his

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Pile Neutron Absorption Cross Sections

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Neutron absorption cross sections for over 50 elements have been measured in the neutron flux of the Argonne heavy water reactor. Measurements were made by observing the oscillating component of reactor power as a neutron absorber sample was oscillated in and out of the central flux of the pile. Calibration was effected with boron.

I. INTRODUCTION

I T was originally suggested by Fermi that neutron absorption cross sections for pile neutrons could be measured by inserting absorbers in the center of a pile in equilibrium and adjusting one of the control rods to compensate for the absorption. The compensating motion, Δl , would then be proportional to the absorption, $n_a\sigma_a$, and could be evaluated in terms of a standard such as boron. This method, termed the "danger coefficient method" (because the absorber was thought of as a poison to the reactor), was applied successfully at Argonne by Wattenberg in the measurement of about 20 elements.

A modification of the "danger" or static method was later suggested by Fermi and Wigner. This method was dynamic in character and consisted in oscillating an absorbing sample in and out of the reacting flux of a pile, while observing the oscillating component of pile power, Δp , and the mean pile power $\bar{p}(\Delta p \ll \bar{p})$. For a thin sample:

$\Delta p \propto \bar{p} n_a \sigma_a$,

where n_a and σ_a are the number of absorbing nuclei and the neutron absorption cross section, respectively.

The apparatus for performing these measurements was developed by a group under the direction of A. Langsdorf at the Argonne National Laboratory. Measurements were made later on 55 elements by the authors.

II. APPARATUS

The equipment will be described in a paper by Langsdorf and his collaborators in a future publication. Briefly it consists of:

(1) A vertical mechanical oscillator which periodically lowers a 75-cc "can" containing the absorbing material into the center of the reacting neutron flux for 10 sec. and then raises the sample out of the flux for 10 sec. The stroke is five feet in length. All parts that oscillate in the reactor flux are made of Dow-Metal FS-1 with the exception of the sample cans, bronze clamp, and graphite bearings.¹

(2) A BF₃ ionization chamber to record both the total current, $i \propto \bar{p}$, and the oscillating current, $\Delta i \propto \Delta p$. This neutron chamber is placed in the thermal column of the reactor, which location is suitable for indicating the power level of the pile.

(3) A bridge circuit (20 sec. sensitivity) with ohmic

¹ Measurement of the neutron absorption cross section of Mg by an all-Al oscillator was shown by Langsdorf and his group to be about 0.07×10^{-24} cm². This approximate value was also confirmed by Wattenberg (Argonne, 1945) and by Goldhaber and Muehlhause (University of Illinois, 1942). Dow metal FS-1 which consists of ~95 percent Mg, five percent Al, and 0.15 percent Mn has therefore an effective neutron absorption cross section of about 0.1 barn and is three times less absorptive per unit volume than is Al.