

## The Vibration-Rotation Bands of the Hydrogen Halides HF, H<sup>35</sup>Cl, H<sup>37</sup>Cl, H<sup>79</sup>Br, H<sup>81</sup>Br and H<sup>127</sup>I

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**ABSTRACT.** The 2-0, 3-0 and 4-0 bands of <sup>1</sup>H<sup>19</sup>F, the 4-0 and 5-0 bands of <sup>1</sup>H<sup>35</sup>Cl and <sup>1</sup>H<sup>37</sup>Cl, the 4-0 band of <sup>1</sup>H<sup>79</sup>Br and <sup>1</sup>H<sup>81</sup>Br, and the 4-0 band of <sup>1</sup>H<sup>127</sup>I were photographed under great dispersion in the infra-red. The molecular constants have been calculated and are summarized in a table.

### § 1. INTRODUCTION

IN the course of a research programme on the structure of polyatomic molecules, whose vibration-rotation spectra in the photographic infra-red permit a definite interpretation of the geometric configuration of the individual atoms in the molecular system, we have also photographed a number of unknown harmonic bands of the diatomic molecules <sup>1</sup>H<sup>19</sup>F, <sup>1</sup>H<sup>35</sup>Cl, <sup>1</sup>H<sup>37</sup>Cl, <sup>1</sup>H<sup>79</sup>Br, <sup>1</sup>H<sup>81</sup>Br and <sup>1</sup>H<sup>127</sup>I. It seemed valuable to us to calculate the constants of these molecules again from the new and improved data.

The bands were photographed in the first and partly also in the second order of a 6-metre grating on special re-sensitized infra-red plates. The dispersion was 2.6 Å. in the first and 1.3 Å. per mm. in the second order. The light-source was either a 1,000-watt pointolite or the sun, using a heliostat. A special mirror arrangement and an infra-red filter was used. A 12-metre long galvanized tube which consisted of several lengths which could be put together served as absorption tube. The light could be sent by mirrors backwards and forwards through the tube up to seven times, so that the maximum length of the absorption path was 84 metres.\* The steel tube was closed at both ends by windows of Plexiglass which is very resistant to the hydrogen halides. The hydrogen halides diffuse a little into the surface of the windows but cause no fogging of the windows. Care had, however, to be taken that when the gases were changed the windows were either replaced or the plates cleaned. This was best accomplished by turning off the first few layers in a lathe and repolishing the surface. The exposures lasted up to 60 hours. The photographs were taken at room temperature (28° C.).

The wavelengths were determined by measuring the plates against iron standard lines photographed in the third or fourth orders of the grating. The accuracy of the determinations may have reached  $\pm 0.01 \text{ cm}^{-1}$ ; the third decimal places are, however, given in the tables. It is difficult to draw definite conclusions about a possible temperature shift of the Fe lines (photographed at the start) relative to the absorption lines during the long exposure times. It is believed that this possible source of error is not important in this case.

\* We are preparing a 25-m.-long absorption tube which will allow a light beam to traverse it up to 40 times. This will correspond to an absorption path of 1,000 m.

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The atmospheric bands which lie in the photographic infra-red region were photographed separately. In this way these lines could be eliminated and a definite determination of the partly superposed absorption bands was greatly simplified.

The gases were prepared according to the usual methods and were purified by repeated re-distillation, and were finally distilled into an evacuated absorption tube.

The 2-0, 3-0 and 4-0 bands of the  $^1\text{H}^{19}\text{F}$ , the 4-0 and 5-0 bands of the  $^1\text{H}^{35}\text{Cl}$  and  $^1\text{H}^{37}\text{Cl}$ , the 4-0 bands of the  $^1\text{H}^{79}\text{Br}$  and  $^1\text{H}^{81}\text{Br}$ , and the 4-0 band of the  $^1\text{H}^{127}\text{I}$  were photographed for the first time. On the other hand, the attempt to find the corresponding harmonic bands of CO failed.

For each molecule the wave-numbers of the new lines, the combination differences for the ground state of all known bands, which gives a measure of the accuracy of the measurements, the calculated vibration levels together with the results of previous investigations and a summary of the newly determined molecular constants are given in the tables.

The molecular constants are calculated with the new values of the fundamental constants according to Birge (1941). Values of wave-numbers are corrected to vacuum. It is believed that the results given here are in some cases more accurate than those published previously owing to the greater dispersion employed here.

§ 2. HYDROGEN FLUORIDE

Besides the vibration-rotation absorption spectra of the diatomic molecules  $^1\text{H}^{35}\text{Cl}$  and  $^1\text{H}^{37}\text{Cl}$ , the spectrum of  $^1\text{H}^{19}\text{F}$  has been investigated most thoroughly in the infra-red. The 1-0 band was measured by Imes (1919) and recalculated by Czerny (1927). Schaefer and Thomas (1923) found that the centre of the 2-0 band, which could not be resolved by them, lies at  $1.27\mu$ . There also exist analyses by Kirkpatrick and Salant (1935) of the 3-0 and 4-0 bands which lie in the photographic infra-red.

Our results for the 2-0, 3-0 and 4-0 bands are given in Tables 1, 2 and 3.

Table 1. 2-0 Band of  $^1\text{H}^{19}\text{F}$

$J$	$R(J)$	$P(J)$
0	7789.730	—
1	7824.742	7710.824
2	7856.833	7666.526
3	7885.894	7619.486
4	7911.830	7569.704

Table 2. 3-0 Band of  $^1\text{H}^{19}\text{F}$

$J$	$R(J)$	$P(J)$
0	11409.047	—
1	11441.206	11331.161
2	11468.679	11285.843
3	11491.449	11235.948
4	11509.490	11181.550
5	11522.781	11122.989
6	11531.282	11060.232
7	11534.920	—

Table 3. 4-0 Band of  $^1\text{H}^{19}\text{F}$

$J$	$R(J)$	$P(J)$
0	14866.625	—
1	14895.680	14790.435
2	14918.894	14743.420
3	14935.820	14690.427
4	14946.702	14631.771
5	14951.654	14567.358

Table 4. Combination Differences for the Ground State,  $v=0$ ,  $^1\text{H}^{19}\text{F}$ .  
 $\Delta_2 F''(J) = R(J-1) - P(J+1)$ 

J	Naudé and Verleger			Kirkpatrick and Salant		Czerny and Imes
	2-0	3-0	4-0	3-0	4-0	1-0
1	123.204	123.204	123.205	123.21	123.20	122.92
2	205.256	205.258	205.253	205.25	205.24	205.21
3	287.129	287.129	287.123	286.95	287.06	286.08
4	—	368.460	368.462	368.27	368.32	366.50
5	—	449.258	449.269	449.57	—	446.78

Table 5. Position of the Vibration Levels,  $^1\text{H}^{19}\text{F}$ 

v	Naudé and Verleger	Kirkpatrick and Salant	Czerny and Imes	Schaefer and Thomas
1	3962.960	—	3962.565	—
2	7751.766	—	—	7874.02
3	11372.574	11372.88	—	—
4	14831.550	14831.68	—	—

Table 6. Molecular Constants of  $^1\text{H}^{19}\text{F}$ 

$B_0 = 20.5352 \text{ cm}^{-1}$	$I_c = 1.3385 \times 10^{-40} \text{ gm.cm}^2$	
$B_1 = 19.7870$	$r_c = 0.9179 \times 10^{-8} \text{ cm.}$	
$B_2 = 19.0249$	$\omega_c = 4143.01 \text{ cm}^{-1}$	
$B_3 = 18.2876$	$\omega_c x_c = 91.69$	
$B_4 = 17.5609$	$\omega_c y_c = 1.03$	
$B_c = 20.9093$	$h_c = 9.68 \times 10^5 \text{ dyne/cm.}$	
$D_c = 0.00108$	Dissoc. energy (computed from $\omega_c, \omega_c x_c$ )	
$\alpha_c = 0.7482$		} = 133.76 kcal/mol.chem. = 5.8 ev.
$\beta_c = 0.0002$		

The discrepancy between the results of Schaefer and Thomas (1923) and ours for the 2-0 band can only be ascribed to the small sensitivity of the method of registration used by them.

### § 3. HYDROGEN CHLORIDE

The 1-0 and 2-0 bands of both isotope molecules in the thermal infra-red were measured by Meyer and Levin (1929). Herzberg and Spinks (1934) studied the 3-0 band in the photographic infra-red. This was the first vibration-rotation spectrum of a diatomic molecule to be thoroughly investigated in this region. Cleaves and Edwards (1935) announced in a short paper the photography of the 4-0 band, but gave no analysis. Lindholm (1942) investigated the pressure broadening of this band without giving detailed data about the molecular constants.

Table 7. 4-0 Band of  $^1\text{H}^{35}\text{Cl}$ 

J	R(J)	P(J)
0	10941.276	—
1	10957.329	10901.918
2	10971.009	10878.608
3	10982.288	10852.957
4	10991.217	10824.972
5	10997.801	10794.691
6	(11002.001)	10762.103

Table 8. 5-0 Band of  $^1\text{H}^{35}\text{Cl}$ 

J	R(J)	P(J)
0	13413.117	—
1	13427.969	13374.368
2	13439.830 s	13350.453
3	13448.721	13323.558
4	13454.632	13293.683
5	13457.586	13260.927

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Table 9. 4-0 Band of  $^1\text{H}^{37}\text{Cl}$

$J$	$R(J)$	$P(J)$
0	10933.759	—
1	10949.804	10894.464
2	10963.451	10871.232
3	10974.738	10845.594
4	10983.664	10817.561
5	10990.220	10787.188

Table 10. 5-0 Band of  $^1\text{H}^{37}\text{Cl}$

$J$	$R(J)$	$P(J)$
0	13404.128	—
1	13418.976	13365.472
2	13430.840	13341.608
3	13439.743 s	13313.777
4	13445.686	13285.005

s = superposed.

Table 11. Combination Differences for the Ground State,  $v=0$ ,  $^1\text{H}^{35}\text{Cl}$

$J$	Naudé and Verleger		Herzberg and Spinks	Meyer and Levin	
	4-0	5-0	3-0	1-0	2-0
1	62.668	62.664	62.626	62.69	63.00
2	104.372	104.411	104.311	104.29	104.16
3	146.037	146.147	145.994	146.03	146.04
4	187.597	187.794	187.507	187.45	187.61
5	229.114	—	228.994	228.87	228.84

Table 12. Combination Differences for the Ground State,  $v=0$ ,  $^1\text{H}^{37}\text{Cl}$

$J$	Naudé and Verleger		Herzberg and Spinks	Mayer and Levin	
	4-0	5-0	3-0	1-0	2-0
1	62.527	62.520	62.599	62.57	62.99
2	104.210	104.199	104.132	104.18	104.03
3	145.890	145.835	145.780	145.83	146.02
4	187.550	—	187.233	187.31	187.52

Table 13. Position of Vibration Levels,  $^1\text{H}^{35}\text{Cl}$

$v$	Naudé and Verleger	Herzberg and Spinks	Meyer and Levin
1	2886.194	—	2885.88
2	5668.526	—	5667.96
3	8347.199	8347.200	—
4	10922.636	—	—
5	13395.204	—	—

Table 14. Position of Vibration Levels,  $^1\text{H}^{37}\text{Cl}$

$v$	Naudé and Verleger	Herzberg and Spinks	Meyer and Levin
1	2883.473	—	2883.87
2	5663.881	—	5663.96
3	8341.182	8341.186	—
4	10915.332	—	—
5	13386.288	—	—

Both the isotope molecules  $^1\text{H}^{35}\text{Cl}$  and  $^1\text{H}^{37}\text{Cl}$ , which differ in their masses but not in their atomic numbers, must have the same force constants and nuclear distances owing to the identity of the electron motions. On the other hand the vibrational frequencies and the rotational terms must be different as a result of their different masses.

In the case of the isotope effect observed here, one has to deal essentially with a vibrational isotope effect on which is superposed a much smaller rotational isotope effect.

By introducing a factor  $\rho = \sqrt{\mu_2/\mu_1}$  the isotope shift due to the vibration can be calculated from

$$\Delta\nu_v = \nu_v^i - \nu_v = (\rho - 1)\omega_e[(v' + \frac{1}{2}) - (v'' + \frac{1}{2})] - (\rho^2 - 1)\omega_e x_e[(v' + \frac{1}{2})^2 - (v'' + \frac{1}{2})^2],$$

where  $\nu_v$  and  $\nu_v^i$  indicate the frequency of the corresponding bands.

Table 15. Molecular Constants for  $^1\text{H}^{35}\text{Cl}$  and  $^1\text{H}^{37}\text{Cl}$ 

	$^1\text{H}^{35}\text{Cl}$	$^1\text{H}^{37}\text{Cl}$
$B_0$	10.4440 $\text{cm}^{-1}$	10.4204 $\text{cm}^{-1}$
$B_1$	10.1445	10.1213
$B_2$	9.8450	9.8221
$B_3$	9.5343	9.5230
$B_4$	9.2615	9.2275
$B_5$	8.9462	8.9197
$B_6$	10.5937	10.5700
$D_e$	0.000533	0.000532
$\alpha_e$	0.2995	0.2992
$\beta_e$	0.000004	0.000004
$I_e$	$2.6409 \times 10^{-40}$ gm.cm <sup>2</sup>	$2.6477 \times 10^{-40}$ gm.cm <sup>2</sup>
$r_e$	$1.2744 \times 10^{-8}$ cm.	$1.2750 \times 10^{-8}$ cm.
$\omega_e$	2990.57 $\text{cm}^{-1}$	2986.50 $\text{cm}^{-1}$
$\omega_e x_e$	52.26	51.50
$\omega_e y_e$	0.06	-0.01
$h_e$	$5.16 \times 10^5$ dyne/cm.	$5.15 \times 10^5$ dyne/cm.
Dissoc. energy	122.28 kcal/mol. chem.	123.75 kcal/mol. chem.
(from $\omega_e, \omega_e x_e$ )	5.30 ev.	5.37 ev.

For the rotational part of the isotope effect, which has the result that the isotope effect of corresponding band lines are not the same but are increasingly shifted, one gets

$$\Delta\nu_r = \nu_r' - \nu_r = (\rho^2 - 1) \left[ \nu_r - \frac{1}{2} \alpha \left\{ (v' + \frac{1}{2})(J' + \frac{1}{2})^2 - (v'' + \frac{1}{2})(J'' + \frac{1}{2})^2 \right\} + D_e \left\{ (J' + \frac{1}{2})^4 - (J'' + \frac{1}{2})^4 \right\} \right].$$

$\nu_r$  denotes the rotational portion of the wave number of a line.

The good agreement of the isotope shifts can be seen from the following table, where the average of the measured displacements for all the lines of the 1-0, 2-0, 3-0, 4-0 and 5-0 bands are compared with the theoretical displacements.

Table 16. Observed and Calculated Vibrational Isotope Shifts in the Infra-red Hydrogen Chloride Bands

Band	Observed	Calculated	Observer
1-0	2.01	2.105	Meyer and Levin
2-0	4.00	4.053	Meyer and Levin
3-0	5.834	5.854	Herzberg and Spinks
4-0	7.490	7.481	Naudé and Verleger
5-0	8.899	8.907	Naudé and Verleger

By determining the factor  $\rho = \sqrt{(\mu/\mu_0)}$  it is possible to obtain an accurate value for the mass ratio of the participating molecules and to compare the value obtained with Aston's value. This determination can be made from the vibrational or the rotational isotope effect, but can also be found by comparison of the molecular constants, for we have, for example,

$$B_e^1 = \rho^2 B_e; \quad \alpha_e^1 = \rho^3 \alpha_e; \quad D_e^1 = \rho^4 D_e.$$

A simple computation shows that Aston's values are verified by the observed isotope effects and, furthermore, that his values are more accurate than assumed by him. Herzberg and Spinks (1934), as well as Jenkins and McKellar (1932), have pointed this out before.

We intend to investigate the isotope effects of the deuterium halides separately.

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§4. HYDROGEN BROMIDE

Plyler and Barker (1933) have photographed and analysed the 1-0 and 2-0 bands of the HBr molecule most recently. The resolution of their arrangement did not, however, suffice to establish independent equations for the isotopic molecules  $^1\text{H}^{79}\text{Br}$  and  $^1\text{H}^{81}\text{Br}$ .

The 4-0 band was the only one which we could photograph with the isotope effect clearly visible. Of the 3-0 band at 13500 Å. only two to three lines of the R branch could be observed, and we could find no absorption of the 5-0 band which lies at 8130 Å.

Table 17. 4-0 Band of  $^1\text{H}^{79}\text{Br}$

<i>J</i>	<i>R(J)</i>	<i>P(J)</i>
0	9709.392	—
1	9722.501	9677.765
2	9733.817	9659.230
3	9743.351	9638.898

Table 18. 4-0 Band of  $^1\text{H}^{81}\text{Br}$

<i>J</i>	<i>R(J)</i>	<i>P(J)</i>
0	9708.020	—
1	9721.123	9676.405
2	9732.484	9657.878
3	9742.048	9637.554

Table 19. Combination Differences for the Ground State  $v=0$ ,  $^1\text{H}^{79}\text{Br}$  and  $^1\text{H}^{81}\text{Br}$

<i>J</i>	Naudé and Verleger		Plyler and Barker	
	4-0 ( $^1\text{H}^{79}\text{Br}$ )	4-0 ( $^1\text{H}^{81}\text{Br}$ )	1-0 ( $^1\text{H}^{79,81}\text{Br}$ )	2-0 ( $^1\text{H}^{79,81}\text{Br}$ )
1	50.162	50.142	50.04	49.97
2	83.603	83.569	83.37	83.30

Table 20. Molecular Constants of  $^1\text{H}^{79}\text{Br}$  and  $^1\text{H}^{81}\text{Br}$

	$^1\text{H}^{79}\text{Br}$	$^1\text{H}^{81}\text{Br}$
$\nu$ (4-0)	9694.495 $\text{cm}^{-1}$	9693.151 $\text{cm}^{-1}$
$B_0$	8.360	8.357
$B_1$	7.454	7.439
$B_2$	8.473	8.471
$\alpha_0$	0.226	0.229
$D_0$	0.000372	0.000378
$\beta_0$	0.000002	0.000003
$I_0$	$3.303 \times 10^{-40}$ gm.cm <sup>2</sup>	$3.304 \times 10^{-40}$ gm.cm <sup>2</sup>
$r_0$	$1.414 \times 10^{-8}$ cm.	$1.414 \times 10^{-8}$ cm.

The  $\omega_x$ ,  $\omega_x x_e$  and  $\omega_c y_e$  values cannot be computed on the basis of these bands, because the data of Plyler and Barker (1933) for the 1-0 and 2-0 bands correspond to an average value for the two bromine isotopes. If one assumes  $\omega_c = 2649.67$  and  $\omega_x x_e = 45.21$  according to Plyler and Barker, one gets  $\nu = 9694.5$  for the 4-0 band, which corresponds to the value found for  $^1\text{H}^{79}\text{Br}$ .

The computed vibrational isotope shift is  $1.34 \text{ cm}^{-1}$ , whereas the average taken over all the lines of the 4-0 band amounts to  $1.35 \text{ cm}^{-1}$ .

§5. HYDROGEN IODIDE

The 1-0 and 2-0 bands of  $^1\text{H}^{127}\text{I}$  were investigated successfully by A. H. and H. H. Nielsen (1935). Just as in the case of the hydrogen bromides, only a few lines of the 4-0 band could be photographed on account of the strong decrease in the intensity of the harmonic bands. Together with the results of Nielsen and Nielsen they suffice, however, to carry out a calculation of the molecular constants.

Table 21. 4-0 Band of  $^1\text{H}^{127}\text{I}$ 

$J$	$R(J)$	$P(J)$
0	8454.972	—
1	8464.976	8430.608
2	8473.514	8416.213
3	8480.608	8400.378

Table 22. Combination Differences for the Ground State  $v=0$ ,  $^1\text{H}^{127}\text{I}$ 

$J$	Naudé and Verleger		Nielsen and Nielsen	
	4-0		1-0	2-0
1	38.759		38.51	39.27
2	64.598		64.22	65.24

Table 23. Position of the Vibrational Levels,  $^1\text{H}^{127}\text{I}$ 

$v$	Naudé and Verleger	Nielsen and Nielsen
1	2230.07	2230.08
2	4380.68	4380.71
3	6451.83	—
4	8443.52	—

Table 24. Molecular Constants of  $^1\text{H}^{127}\text{I}$ 

$B_0=6.460 \text{ cm}^{-1}$	$I_0=4.272=10^{-40} \text{ gm.cm}^2$
$B_1=5.729$	$r_e=1.604 \times 10^{-8} \text{ cm.}$
$B_v=6.551$	$\omega_c=2309.53 \text{ cm}^{-1}$
$\alpha_e=0.183$	$\omega_e x_e=39.73$
$D_0=0.000213$	$k=3.14 \times 10^8 \text{ dyne/cm.}$
$\beta_c=0.000003$	Dissoc. energy } $=95.93 \text{ kcal/mol. chem.}$ (from $\omega_c, \omega_e x_e$ ) } $=4.2 \text{ ev.}$

According to theoretical considerations it could be expected that the intensities of the harmonic bands of HF would diminish increasingly as one proceeds successively to HCl, HBr and HI, and that the harmonic bands of the last molecule would not be observed in the region which we were able to photograph. Actually, however, it was possible to obtain plates also of the 4-0 band of HI.

An accurate comparison of the intensities of the four hydrogen halides of a given harmonic band has not been carried out. However, considering the fact that for  $^1\text{H}^{35}\text{Cl}$ , and even for  $^1\text{H}^{37}\text{Cl}$ , the highest harmonic vibrational bands were found and that their intensities were not so much less than could be expected according to theoretical considerations based on the intensity of the corresponding HF bands, it seems as if this missing intensity difference can be understood by an association of a part of the HF molecules to form double molecules. A band which would correspond to  $(\text{HF})_2$  could, however, not be observed with certainty. The 4-0 bands of HBr and HI are indeed substantially weaker than the corresponding bands of HCl and HF, but nevertheless, especially in the case of HI, not so weak as would be expected from the suspected approximate homopolar character of the bond of this molecule. The non-appearance of the CO bands in this spectral region remains completely inexplicable in this connection, for their intensities should have sufficed according to the above considerations.

After completing a larger absorption installation it is hoped to extend the above results and to continue the investigation of polyatomic molecules. By

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means of a shorter absorption tube we have already found new or additional absorption bands in the case of methyl cyanide ( $H_3C-C\equiv N$ ), azomethane ( $H_3C-N=N-CH_3$ ) and methyl acetylene ( $H_3C-C\equiv CH$ ).

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REFERENCES

BIRGE, R. T., 1941, *Rev. Mod. Phys.*, **13**, 233.  
 CLEAVES, A. R., and EDWARDS, C. W., 1935, *Phys. Rev.*, **48**, 850.  
 CZERNY, M., 1927, *Z. Phys.*, **45**, 476.  
 HERZBERG, C., and SPINKS, J. W. T., 1934, *Z. Phys.*, **89**, 474.  
 IMES, E. S., 1919, *Astrophys. J.*, **50**, 251.  
 JENKINS, E. A., and MCKELLAR, A., 1932, *Phys. Rev.*, **39**, 549.  
 KIRKPATRICK, D. E., and SALANT, E. O., 1935, *Phys. Rev.*, **48**, 945.  
 LINDHOLM, E., 1942, *Dissertation*, Stockholm.  
 MEYER, C. F., and LEVIN, A. D., 1929, *Phys. Rev.*, **34**, 44.  
 NIELSEN, A. H., and NIELSEN, H. H., 1935, *Phys. Rev.*, **47**, 585.  
 PLYLER, E. K., and BARKER, E. F., 1933, *Phys. Rev.*, **44**, 984.  
 SCHAEFER, CL., and THOMAS, M., 1923, *Z. Phys.*, **12**, 330.

Calculation of the Correction for Instrumental Broadening in X-ray Diffraction Lines

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ABSTRACT. A new numerical procedure, based on relaxation methods, for calculating the correction for instrumental broadening in x-ray diffraction lines has been evolved. The corrected integral breadth and the true line profile are obtained without restrictive assumptions. The calculations for a practical example are given.

§1. INTRODUCTION

IN x-ray line-broadening studies, it is required to correct for the broadening due to 'instrumental' factors in the measured intensity distribution curve of the line; the line broadening obtained under similar geometrical conditions from an annealed specimen is often taken as a measure of this instrumental broadening. The problem has been clearly stated by Jones (1938) and involves solving the simple integral equation (1) given below. Recently, Stokes (1948) has published a method of solution, using Fourier analysis, which avoids the special assumptions regarding the form of the solution that have been made by previous workers. The present paper will describe briefly the numerical method that the author has used for solving the problem. It is very simple and direct, although in its present form it may take a slightly longer time than Stokes' method when means of rapid Fourier analysis are available. However, it may be of interest to describe it since it has the same general applicability, yielding the true line shape as well as its breadth.

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