Acta Cryst. (1956). **9**, 897

The Structure of Potassium Dithionate

By E. Stanley*

Division of Pure Physics, National Research Council, Ottawa, Canada

(*Received* 25 *April* 1956)

The structure of potassium dithionate, space group $P321$, $a = 9{\cdot}785 \pm 0{\cdot}001$, $c = 6{\cdot}295 \pm 0{\cdot}001$ Å, has been refined using $F_o - F_c$ methods. The observed structure factors for the $hk.0$ and $h0.l$ reflexions were obtained from precession photographs taken with Mo $K\alpha$ radiation. The final R values for the $hk.0$ and $h0.l$ reflexions are 0·08 and 0·07 respectively. The S–S bond length is $2{\cdot}15 \pm 0{\cdot}02$ Å and the S–O bond lengths $1{\cdot}43 \pm 0{\cdot}05$ Å. Each potassium ion is bound to six oxygen atoms at a distance of $2{\cdot}83 \pm 0{\cdot}04$ Å. The two non-equivalent dithionate ions have symmetry 32 and 3. In the former the projected angle between the terminal oxygen groups is $23{\cdot}5 \pm 1°$. In the latter the angle is $54{\cdot}5 \pm 1°$. This rotation about the S–S bond does not appear to distort the ion in any other way. The refined structure is compared with those given by Huggins and by Helvig, and is found to be closer to the former.

Introduction

Quantitative determinations of the structure of potassium dithionate have been made by Huggins & Frank (1931), later modified by Huggins (1933), and by Helvig (1932). These differ in detail; in particular the orientations of the oxygen atoms about the S–S bonds of the dithionate ions are different. There was little to choose between the two proposed structures from the agreement between the F_o and F_c values given by the authors. The K–O interionic bond lengths are more uniform and of the expected magnitude in the modified Huggins & Frank structure, which is very similar, in general, to that of rubidium dithionate proposed by Barnes & Wendling (1938).

There are two non-equivalent dithionate ions in the structure of potassium dithionate, both of which lie with their axes (S–S bond) along a threefold axis parallel to c. This feature provides an opportunity for accurate measurement of the S–S bond in the dithionate ion.

Preliminary measurements

The space group, $P321$ (No. 150 of *International Tables*, 1952), was determined by Barnes & Helvig (1931) and by other investigators. The unit-cell dimensions now have been more accurately determined by the method of Farquhar & Lipson (1947) as

$$a = 9{\cdot}785 \pm 0{\cdot}001, \quad c = 6{\cdot}295 \pm 0{\cdot}001 \text{ Å}.$$

New visual intensity measurements have been made on precession photographs of the $hk.0$ and $h0.l$ reflexions taken using the same spherical crystal with Mo $K\alpha$ radiation. These intensities have been corrected for absorption using the figures given by Evans & Ekstein (1952), and for geometrical factors using the values of Waser (1951).

Refinement of the structure

Comparison of the new observed structure factors of the $hk.0$ reflexions with the calculated structure factors for the previous determination appeared to favour the modified Huggins & Frank model. The Fourier projection of electron density on (00.1), using the observed structure-factor magnitudes and the phases calculated from the modified Huggins & Frank model, gave a well resolved map in good agreement with the model. The projection was refined using the $F_o - F_c$ method of Cochran (1951). Individual isotropic temperature factors were used for each atom during the later stages of refinement. The final value of R was 0·08. The observed and calculated structure factors for the [00·1] zone are given in Table 1.

The Fourier projection of electron density on (01.0) was calculated, using the signs determined for the x coordinates obtained at an early stage of the refinement of the [00.1] zone and the z coordinates of the modified Huggins & Frank model with the new observed structure-factor magnitudes. This gave a reasonably well resolved map from which improved atomic coordinates were obtained. Refinement was continued, independently of the [00.1] zone, using the $F_o - F_c$ method. Structure factors were calculated using the symmetry ($\bar{1}$) of the projection only, and individual isotropic temperature coefficients were used for the various atoms during the later stages of refinement. The final value of R was 0·07. The observed and calculated structure factors for the [01.0] zone are given in Table 2.

The atomic scattering curves used throughout were the oxygen curve of McWeeny (1951) modified at low values of $\sin\theta/\lambda$ to extrapolate to $Z_O = 8{\cdot}33$ (since

---

* National Research Laboratories Postdoctorate Fellow. Present address: Department of Physics, College of Science and Technology, Manchester 1, England.

Table 1. *Observed and calculated structure factors for hk.0 reflexions*

hk.l	$\lvert F_c \rvert$	α (°)	$\lvert F_o \rvert$	hk.l	$\lvert F_c \rvert$	α (°)	$\lvert F_o \rvert$	hk.l	$\lvert F_c \rvert$	α (°)	$\lvert F_o \rvert$
10.0	0·0	0	< 2·4	71.0	44·5	11	42·1	63.0	30·6	342	33·0
20.0	8·9	0	11·1	81.0	17·4	126	15·1	73.0	15·1	7	10·9
30.0	94·2	0	88·8	91.0	10·1	235	11·1	83.0	11·0	338	11·6
40.0	7·3	0	10·2	10,1.0	18·8	16	20·8	93.0	15·0	318	15·1
50.0	20·8	0	18·8					10,3.0	11·8	339	9·2
60.0	67·4	0	66·8	22.0	18·6	218	13·8				
70.0	22·2	0	19·9	32.0	33·0	274	34·9	44.0	35·9	20	37·6
80.0	15·2	0	14·5	42.0	19·0	137	22·8	54.0	29·4	117	28·4
90.0	17·9	0	20·6	52.0	45·0	3	45·1	64.0	6·6	264	6·5
10,0.0	19·3	0	19·9	62.0	3·3	124	< 6·3	74.0	24·2	22	22·5
11,0.0	10·3	0	5·9	72.0	13·5	150	17·3	84.0	7·9	194	9·6
				82.0	27·9	15	26·7				
11.0	78·5	357	72·5	92.0	9·2	218	7·2	55.0	28·6	341	31·0
21.0	20·0	120	21·9	10,2.0	4·5	153	5·2	65.0	5·0	274	3·3
31.0	46·4	273	44·7					75.0	8·2	126	7·4
41.0	15·6	354	19·9	33.0	59·0	343	60·9	85.0	23·7	13	24·7
51.0	35·9	110	32·8	43.0	12·4	324	14·0				
61.0	30·4	255	28·6	53.0	15·5	305	15·6	66.0	21·7	286	20·2

Table 2. *Calculated and observed structure factors for h0.l reflexions*

hk.l	F_c	$\lvert F_o \rvert$	hk.l	F_c	$\lvert F_o \rvert$	hk.l	F_c	$\lvert F_o \rvert$	hk.l	F_c	$\lvert F_o \rvert$
10.0	− 2·0	< 2·2	$\bar{4}0.2$	0·0	< 5·4	$\bar{9}0.4$	− 1·1	< 6·4	$\bar{7}0.6$	+12·4	12·8
20.0	+ 9·7	10·4	$\bar{3}0.2$	+48·2	49·2	$\bar{8}0.4$	+ 6·8	< 6·8	$\bar{6}0.6$	− 0·1	< 6·8
30.0	+90·8	91·6	$\bar{2}0.2$	−24·0	22·2	$\bar{7}0.4$	+12·0	10·1	$\bar{5}0.6$	+28·0	27·3
40.0	+ 7·8	8·7	$\bar{1}0.2$	+35·8	36·5	$\bar{6}0.4$	+ 8·1	8·0	$\bar{4}0.6$	+10·4	9·6
50.0	+20·5	17·3	00.2	−26·3	25·4	$\bar{5}0.4$	− 5·9	5·5	$\bar{3}0.6$	+ 9·4	10·6
60.0	+64·8	65·3	10.2	−60·2	60·4	$\bar{4}0.4$	+21·8	19·2	$\bar{2}0.6$	+23·8	23·4
70.0	+18·9	18·5	20.2	+22·6	25·4	$\bar{3}0.4$	+28·8	30·7	$\bar{1}0.6$	+ 3·3	< 6·8
80.0	+13·2	13·9	30.2	+42·4	43·6	$\bar{2}0.4$	− 4·5	6·0	00.6	+25·0	25·8
90.0	+15·2	16·4	40.2	+12·9	14·0	$\bar{1}0.4$	− 1·5	< 5·4	10.6	+16·4	13·4
10,0.0	+16·0	17·8	50.2	+22·2	25·4	00.4	+56·3	53·5	20.6	+10·5	11·6
11,0.0	+ 7·0	6·0	60.2	−16·1	17·1	10.4	+13·5	12·5	30.6	+16·9	17·3
			70.2	− 0·9	< 6·6	20.4	− 0·9	< 5·6	40.6	+26·8	26·4
$\overline{11}$,0.1	+ 0·3	< 6·2	80.2	+18·3	18·0	30.4	+24·7	26·2	50.6	+16·1	15·6
$\overline{10}$,0.1	+ 6·0	5·7	90.2	−10·6	13·3	40.4	−15·3	20·2	60.6	+ 0·6	< 6·8
$\bar{9}0.1$	− 7·4	7·0	10,0.2	+11·1	9·6	50.4	+ 6·8	9·4	70.6	+20·1	19·4
$\bar{8}0.1$	+19·0	19·9	11,0.2	+11·8	12·5	60.4	+ 8·4	8·4	80.6	+11·0	8·4
$\bar{7}0.1$	− 0·3	< 6·6				70.4	+ 8·4	10·6			
$\bar{6}0.1$	−10·3	11·3	$\overline{11}$,0.3	+ 7·6	6·9	80.4	+14·2	14·5	$\bar{7}0.7$	− 6·1	5·7
$\bar{5}0.1$	+28·8	31·9	$\overline{10}$,0.3	−15·9	18·3	90.4	− 7·8	8·6	$\bar{6}0.7$	+ 1·1	< 5·6
$\bar{4}0.1$	− 1·9	< 5·2	$\bar{9}0.3$	− 1·9	< 6·6	10,0.4	+ 3·7	< 6·6	$\bar{5}0.7$	+11·9	10·1
$\bar{3}0.1$	−44·1	38·4	$\bar{8}0.3$	+14·9	17·1				$\bar{4}0.7$	− 5·8	5·0
$\bar{2}0.1$	+36·0	37·4	$\bar{7}0.3$	−41·6	38·6	$\bar{9}0.5$	+ 3·4	5·8	$\bar{3}0.7$	+ 9·8	11·3
$\bar{1}0.1$	+31·2	32·4	$\bar{6}0.3$	− 9·0	8·2	$\bar{8}0.5$	+ 8·2	7·6	$\bar{2}0.7$	+ 6·5	5·8
00.1	−16·2	16·8	$\bar{5}0.3$	+42·8	41·4	$\bar{7}0.5$	+ 0·7	< 6·0	$\bar{1}0.7$	− 2·9	< 7·0
10.1	+ 6·1	5·7	$\bar{4}0.3$	−60·3	55·4	$\bar{6}0.5$	+11·8	12·3	00.7	− 4·7	< 7·0
20.1	+55·0	60·2	$\bar{3}0.3$	+ 2·7	< 5·4	$\bar{5}0.5$	+ 6·1	5·8	10.7	− 3·9	< 7·0
30.1	+27·9	23·8	$\bar{2}0.3$	+34·8	30·6	$\bar{4}0.5$	− 8·3	6·9	20.7	+ 5·3	7·2
40.1	−15·2	14·8	$\bar{1}0.3$	−80·9	80·6	$\bar{3}0.5$	+10·0	8·7	30.7	+11·4	12·8
50.1	+49·2	50·6	00.3	−11·0	10·6	$\bar{2}0.5$	+ 0·4	< 6·2	40.7	−11·3	11·3
60.1	− 3·7	< 6·4				$\bar{1}0.5$	+16·2	18·1	50.7	−10·5	10·5
70.1	−14·0	17·6	10.3	− 2·2	< 4·8	00.5	+30·3	31·6	60.7	+ 2·3	< 5·6
80.1	+30·6	28·8	20.3	−27·9	29·6	10.5	−15·9	14·7	70.7	− 6·0	6·5
90.1	+ 0·5	< 6·8	30.3	−16·9	17·1	20.5	+27·8	27·4			
10,0.1	+ 3·8	< 6·6	40.3	−36·0	33·0	30.5	+ 7·8	9·6	$\bar{4}0.8$	− 7·2	7·4
11,0.1	+ 7·0	7·7	50.3	− 5·1	< 6·2	40.5	− 8·8	10·3	$\bar{3}0.8$	+17·9	16·6
			60.3	−11·7	12·2	50.5	+26·5	27·6	$\bar{2}0.8$	− 2·2	< 6·2
$\overline{11}$,0.2	+ 6·2	7·2	70.3	− 3·3	< 6·6	60.5	+12·5	13·2	$\bar{1}0.8$	− 5·0	5·4
$\overline{10}$,0.2	+14·3	14·2	80.3	−11·8	12·2	70.5	−16·1	16·9	00.8	+21·0	20·1
$\bar{9}0.2$	−13·6	13·7	90.3	− 6·7	6·9	80.5	+16·1	16·4	10.8	− 3·1	< 6·4
$\bar{8}0.2$	+ 4·1	< 6·8	10,0.3	− 4·0	3·8	90.5	+ 5·6	6·0	20.8	− 6·7	< 6·2
$\bar{7}0.2$	+25·2	26·1	11,0.3	− 9·2	10·6				30.8	+13·2	12·2
$\bar{6}0.2$	−13·8	15·0				$\bar{8}0.6$	+17·7	16·4	40.8	− 3·0	< 5·4
$\bar{5}0.2$	+ 2·1	< 6·0	$\overline{10}$,0.4	+14·8	14·0						

all the oxygen atoms in the divalent dithionate ion appear to play similar roles in the structure it was considered appropriate to share the charge equally amongst them), the sulphur curve of Viervoll & Ögrim (1949) and the potassium ion curve given in *Internationale Tabellen* (1935).

Atomic coordinates and accuracy

A practical measure of the accuracy of the atomic coordinates can be obtained from the [01·0] projection, which exhibits the symmetry $\bar{1}$ and which was refined using this restriction only. Atoms not in special positions should be arranged in groups of three with the same z coordinate and with the sum of the x coordinates of the three atoms in the group equal to zero. Deviations of the z coordinates from the mean value for the three independent groups of three oxygen atoms have the r.m.s. value of 0·016 Å. Assuming that the error in the x coordinate of each oxygen atom is the same within a group, the r.m.s. error in the x coordinate of an oxygen atom is 0·027 Å.

Two independent estimates of the intensities in the [01.0] zone gave a value of $\langle(\Delta F_o)^2\rangle^{\frac{1}{2}}$ = 1·41 electrons, and the value of $\langle(|F_o|-|F_c|)^2\rangle^{\frac{1}{2}}$ for the same zone was 1·74 electrons. Using the mean of these two figures (1·58 electrons) in the formula given by Booth (1947) gives 0·017 Å for the standard deviation of an oxygen coordinate in the [01.0] zone. The corresponding figures for the [00.1] zone were $\langle(\Delta F_o)^2\rangle^{\frac{1}{2}}$ = 2·07 and $\langle(|F_o|-|F_c|)^2\rangle^{\frac{1}{2}}$ = 2·51 electrons. Using the mean value (2·29 electrons) in Booth's formula gives the standard deviation in an oxygen coordinate in the [00.1] zone as 0·020 Å.

The r.m.s. deviation between the x coordinates of the oxygen atoms from the two independently refined zones is 0·013 Å.

Although the space group requires the sulphur atoms to lie on the threefold axes, i.e. in the positions $(0, 0, z)$ etc. and $(\frac{1}{3}, \frac{2}{3}, z)$ etc. and the potassium ions on the twofold axes at $(x, 0, 0)$ etc., the symmetry of the [01.0] projection does not impose such restrictions on the atomic peak positions. The difference maps showed some gradient perpendicular to the c axis at the positions of the sulphur atoms and perpendicular to the a axis at the positions of the potassium ions. This gradient, even in the early stages of refinement, was too small to justify any movement of the atoms concerned.

The indications are, therefore, that the r.m.s. error in the coordinate of an oxygen atom does not exceed 0·020 Å. Assuming that the error is inversely proportional to the atomic number, the corresponding r.m.s. errors for a coordinate of a sulphur atom and a potassium ion are 0·010 Å and 0·009 Å respectively.

Discussion of the structure

The final coordinates are given in Table 3 and a diagram of the structure projected on (00.1) is shown in Fig. 1. The z coordinates of the oxygen atoms are the mean values for each group of three. The x coordinates are the mean values for the [00.1] and [01.0] projections. The z coordinates of the sulphur atoms were obtained for the [01.0] projection and there was no difference between the refined x coordinates of the potassium ions in the two projections. The values of the isotropic temperature coefficients used in each projection are also given in Table 3. The figures for the oxygen atoms in the [01.0] projection are given in order of increasing magnitude. In all cases this is the same as the order of decreasing projected distance from the oxygen atom to the axis of the ion. This probably indicates that the oscillation of the oxygen atoms are about the axis of the ion rather than in any other direction. The only other atom showing large thermal vibration is the potassium ion at 0·292, 0, ½, etc. The values of ΔB suggest that this atom is vibrating in a plane perpendicular to the a axis.

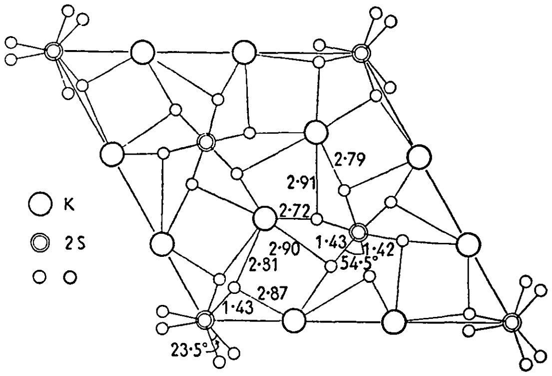

Fig. 1. The structure of $K_2S_2O_6$ projected on (00.1).

The differences between the present structure and

Table 3. *Atomic coordinates of the refined structure*

No. of atoms	Atom	Position*	Coordinates	$\Delta B_{[00.1]}$ (Å²)	$\Delta B_{[01.0]}$ (Å²)		
2	S_1	(*c*)	(0, 0, 0·171) etc.	0·0		0·2	
2	S_2	(*b*)	(⅓, ⅔, 0·261) etc.	0·0		0·1	
2	S_3	(*b*)	(⅓, ⅔, 0·602) etc.	0·0		0·1	
3	K_1^+	(*e*)	(0·617, 0, 0) etc.	0·0	0·0		0·2
3	K_2^+	(*f*)	(0·292, 0, ½) etc.	0·4	0·8		0·5
6	O_1	(*g*)	(0·155, 0·123, 0·231) etc.	1·0	0·2	0·2	0·7
6	O_2	(*g*)	(0·207, 0·514, 0·202) etc.	1·0	0·7	0·7	1·4
6	O_3	(*g*)	(0·174, 0·624, 0·659) etc.	1·0	0·7	1·2	1·2

* The positions are identified by the letters given in *International Tables* (1952).

Table 4. *Summary of differences between present and previous determinations*

		A		*B*	
Atom	Parameter	Mean	Max.	Mean	Max.
S	*z*	0·07 Å	0·12 Å	0·07 Å	0·12 Å
K	*x*	0·10	0·12	0·10	0·12
O	*z*	0·01	0·01	0·05	0·07
	x	0·08	0·13	0·30	0·43

A: Difference between present structure and that of Huggins & Frank (modified).
B: Difference between present structure and that of Helvig.

the previous determination are summarized in Table 4. The differences between the *z* coordinates of the sulphur atom and the *x* coordinates of the potassium ions are of the order 0·1 Å. The S–S bond is larger than that previously obtained. The *z* coordinates of the oxygen atoms are very close to those in the Huggins & Frank structure and differ by only 0·05 Å from those of the Helvig structure. The most marked difference is between the *x* coordinates of the oxygen atoms in the Helvig structure and those in the present determination: these differ by as much as 0·4 Å. The Huggins & Frank oxygen *x* coordinates differ by the order of 0·1 Å from those obtained here.

The dimensions of the two non-equivalent dithionate ions, which have symmetry 32 and 3, are given in Table 5. The difference between them is restricted to the relative orientation of the terminal oxygen groups about the S–S bond as axis. The S–S and S–O bond lengths and the S–S–O bond angle are sensibly the same. The rotation of the terminal oxygen atoms in the dithionate ion centred at the origin through 36·5° from the presumed equilibrium positions in which the ion would be expected to have the symmetry $\bar{3}$, although there is no known example of the ion exhibiting this symmetry, seems to have no effect on the remainder of the bond lengths and bond angles within the ion.

Table 5. *Dimensions of the two non-equivalent dithionate ions*

	Length (Å)		Angle (°)
S_1–S_1	2·15±0·02	S_1–S_1–O	105 ±1
S_2–S_3	2·14±0·02	O_1–S–O_1*	23·5±1
S_1–O_1	1·43±0·05	S_2–S_3–O_3	104 ±1
S_2–O_2	1·42±0·05	S_3–S_2–O_2	105 ±1
S_3–O_3	1·43±0·05	O_2–S–O_3*	54·5±1

* Projected.

Each potassium ion is bound ionically to six oxygen atoms and each oxygen atom is associated with two potassium ions. The mean K–O interionic distance is 2·83 Å and the extreme values are 2·91 and 2·72 Å. The standard deviation of a K–O bond length is σ(K–O) = 0·04 Å. The distribution of the deviation of the observed bond lengths from the mean is: three less than σ(K–O), two between σ(K–O) and 2σ(K–O) and one between 2σ(K–O) and 3σ(K–O). There seems no ground for considering the bond lengths other than equal.

The S–S bond length of 2·15 Å is between the extreme values that have been published for this bond length in this ion. The value of 2·08 Å has been obtained by Stanley (1953) in $NaK_5Cl_2(S_2O_6)_2$ and in $NaK_2Cl(S_2O_6)$, and by Barnes & Wendling (1938) in $Rb_2S_2O_6$ (this last determination was based on qualitative data only). In $BaS_2O_6.2H_2O$ (García Blanco, Gomis & Abbad, 1953) the length of the S–S bond is 2·17 Å. Martínez, García-Blanco & Rivoir (1956) report 2·16 Å for the S–S bond length in sodium dithionate dihydrate. In barium pentathionate (Foss, Furburg & Zachariasen, 1954) and in barium selenopentathionate (Foss & Tjomsland, 1954) the length of the terminal S–S bond is 2·12 and 2·13 Å respectively. The value 2·15 Å compares reasonably well with the values obtained in other types of compound, e.g. 2·11 Å in caesium hexasulphide (standard error 0·03 Å) (Abrahams & Grison, 1953) and 2·15 in *pp*′-dibromodiphenyldisulphide (Toussaint, 1945).

I am indebted to Dr W. H. Barnes for suggesting the problem and for his continued support of the work, and to Mrs M. E. Pippy for assistance with the calculations.

References

Abrahams, S. C. & Grison, E. (1953). *Acta Cryst.* **6**, 206.

Barnes, W. H. & Helvig, G. V. (1931). *Canad. J. Res.* **4**, 565.

Barnes, W. H. & Wendling, A. V. (1938). *Z. Kristallogr.* **99**, 153.

Booth, A. D. (1947). *Proc. Roy. Soc.* A, **190**, 482.

Cochran, W. (1951). *Acta Cryst.* **4**, 408.

Evans, H. T. & Ekstein, M. G. (1952). *Acta Cryst.* **5**, 540.

Farquhar, M. C. M. & Lipson, H. (1947). *Proc. Phys. Soc., Lond.* **58**, 200.

Foss, O., Furburg, S. & Zachariasen, H. (1954). *Acta chem. scand.* **8**, 473.

Foss, O. & Tjomsland, O. (1954). *Acta chem. scand.* **8**, 1701.

García-Blanco, S., Gomis, V. & Abbad, M. (1953). *An. Soc. esp. Fis. Quim.* (A), No. 3–4, 114.

Helvig, G. V. (1932). *Z. Kristallogr.* **83**, 485.

Huggins, M. L. (1933). *Z. Kristallogr.* **86**, 384.

Huggins, M. L. & Frank, G. O. (1931). *J. Min. Soc. Am.* **16**, 580.

Internationale Tabellen zur Bestimmung von Kristallstrukturen (1935). Berlin: Borntraeger.

International Tables for X-ray Crystallography (1952). Birmingham: Kynoch Press.

McWeeny, R. (1951). *Acta Cryst.* **4**, 513.

Martínez, S., García-Blanco, S. & Rivoir, L. (1956). *Acta Cryst.* **9**, 145.

Stanley, E. (1953). *Acta Cryst.* **6**, 187.

Toussaint, J. (1945). *Bull. Soc. chim. Belg.* **54**, 319.

Viervoll, H. & Ögrim, O. (1949). *Acta Cryst.* **2**, 277.

Waser, J. (1951). *Rev. Sci. Instrum.* **22**, 563, 567.