

## Powder Refinement of Carbonyl Sulphide

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### Abstract

The crystal structure of carbonyl sulphide (COS) at 90 K has been reinvestigated using the neutron powder diffraction technique. The structure is rhombohedral, space group  $R3m$ , with unit-cell parameters  $a = 4.063(3) \text{ \AA}$  and  $\alpha = 98.81(3)^\circ$ ;  $R = 0.11$  for 742 independent observations. There is one molecule per unit cell, aligned along the [111] crystallographic axis. The bond lengths have been determined as  $1.21(3)$  and  $1.51(3) \text{ \AA}$  for the O–C and C–S distances respectively.

### Introduction

The first determination of the structure of solid COS was made by Vegard (1931), who reported the space group, unit-cell parameters and the atomic positions. The O–C and C–S bond lengths derived from Vegard's parameters are  $1.10$  and  $1.97 \text{ \AA}$  respectively. These are in contrast to generally accepted modern values and therefore a redetermination is timely. The simple molecular and crystal structure reported for COS makes it a favourable solid for detailed studies of its lattice dynamics and the present determination of the complete molecular structure was undertaken as a preliminary to such an investigation.

### Experimental

The polycrystalline sample of COS was produced by condensing the gas (supplied by Matheson with purity  $\sim 97.5\%$ ) into a vanadium sample can held at a temperature just above the melting point of COS ( $135 \text{ K}$ ). When the can was full, a polycrystalline solid was formed by quenching the liquid COS in liquid nitrogen. The sample-can dimensions were  $15 \text{ mm}$  diameter and  $70 \text{ mm}$  length. The quality of the polycrystalline sample was investigated by measuring the peak intensity of the  $(1\bar{1}0)$  Debye–Scherrer peak as a function of sample

orientation about the cylindrical axis (*i.e.* an axis perpendicular to the scattering plane). Measurements of the peak intensity were made at  $10^\circ$  intervals about the axis, and were distributed about their mean value with a standard deviation of  $8\%$ . The sample was rotated continuously during the experiment to improve the powder 'averaging', and the error in the experimental intensity due to the crystalline nature of the sample is then  $\sim 1\%$ .

The powder diffraction measurements were made with the C5 triple-axis spectrometer, operated in a two-axis mode, at the NRU reactor, Chalk River. The monochromator planes were Ge(113) and the incident neutrons, scattered at  $57.05^\circ$ , had a wavelength of  $1.629 \text{ \AA}$ . Soller-slit collimators with horizontal divergences of  $0.44$  and  $0.47^\circ$  were placed before and after the COS sample respectively. The resolution width of the spectrometer was determined by calibration with a sample of polycrystalline aluminium. The full width at half maximum,  $\Gamma$  (in degrees), of a Debye–Scherrer peak is assumed to be given by  $\Gamma^2 = u \tan^2 \theta + v \tan \theta + w$ , where  $2\theta$  is the scattering angle and  $u, v, w$  are spectrometer constants. Initial values for these constants were determined by fitting this expression to the observed widths of the Debye–Scherrer peaks of the aluminium sample. The intensity of the diffracted neutrons was measured as a function of scattering angle in steps of  $0.1^\circ$  from  $15$  to  $100^\circ$ . The counting time at each point was  $\sim 70 \text{ s}$  (determined by a beam monitor) and the specimen temperature was  $90 \text{ K}$ .

26 Debye–Scherrer peaks with Miller indices ranging from  $100$  to  $311$  were measured, although many of the higher-index peaks were not completely resolved. The experimental scattered neutron distribution is shown by the points in Fig. 1.\* The COS gas probably

\* The numerical intensity of each measured point on the difference profile, as a function of scattering angle, has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36535 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

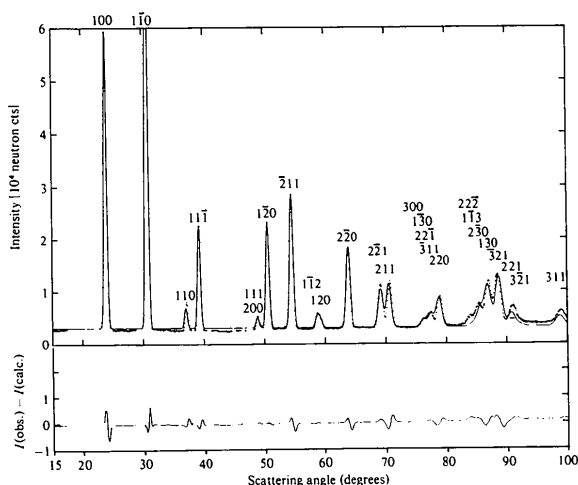


Fig. 1. Neutron intensity as a function of scattering angle,  $2\theta$ . The (110) Debye-Scherrer peak at  $2\theta \approx 30^\circ$  has an intensity of  $1.1 \times 10^5$  neutron counts. Below the scan is the difference plot,  $I(\text{obs.}) - I(\text{calc.})$ , in units of  $10^4$  neutron counts. The gaps in this plot show the regions excluded due to impurity scattering.

contained  $\text{CO}_2$ ,  $\text{CS}_2$  and  $\text{H}_2\text{S}$  as impurities and several impurity peaks were observed. The data in the vicinity of these peaks were omitted in the analysis and are not shown in Fig. 1. The intensity of the largest impurity peak was only  $\sim 1\%$  of the intensity of the largest COS peak and so the presence of the impurities is not expected to affect the analysis of the COS data.

### Analysis

The structure of COS was refined from the powder data by means of the program *EDINP* (Pawley, 1980). In the refinement the first variable parameter introduced was the scale factor, after which the flat background and the effective zero of the scattering-angle scale were added. Successive refinement cycles introduced the unit-cell parameters,  $a$  and  $\alpha$ , the two bond lengths, then the three peak-width parameters  $u, v, w$ , and finally the overall isotropic temperature factor. This made, in all, eleven parameters to be refined in the final cycles. The final values of parameters with their errors are given in Table 1. All data points had unit weights in the refinement.  $R$  is given by  $R = \sum_{i=1}^N |y_i(\text{obs.}) - y_i(\text{calc.})| / \sum_{i=1}^N y_i(\text{obs.})$ , where  $y_i(\text{obs.})$  is the observed intensity at the  $i$ th point in the scan and  $y_i(\text{calc.})$  is the calculated intensity. The sum excludes the regions contaminated by impurity scattering. The least-squares residual is  $R_w = \sum_{i=1}^N w_i [y_i(\text{obs.}) - y_i(\text{calc.})]^2$  (all  $w_i = 1$ ). The standard deviations quoted in Table 1 are derived from the least-squares matrix,  $\mathbf{A}$ , and are defined by:  $\sigma_i^2 = (\mathbf{A}^{-1})_{ii} R_w / (N - n)$ , where  $N (= 742)$  is the number of statistically independent observations in the scan and  $n (= 11)$  the number of refinement variables. Sakata &

Cooper (1979) have suggested that standard deviations derived from profile refinement analysis may be seriously underestimated, but there is some disagreement over the number which should be used as 'statistically independent observations' in profile refinement. It has been argued (Pawley, 1980) that a more realistic number to use in place of  $N$  in the definition of  $\sigma_i^2$ , especially for the structural parameters, is 'the equivalent number of reflections,  $N_e$ ' defined by  $N_e = N/\Delta$ , where  $\Delta$  is the number of steps in the mean width at half height of a Debye-Scherrer peak in the scan. In the present experiment  $\Delta = 19$  and using  $N_e$  rather than  $N$  in the definition for  $\sigma$ , the standard deviations for the structural parameters become  $\sigma(\text{O}-\text{C}) = 0.03$  and  $\sigma(\text{S}-\text{C}) = 0.03 \text{ \AA}$ . Similarly all the standard deviations in Table 1 are increased by a factor of five if  $N_e$ , rather than  $N$ , is used.

It will be noted that at large scattering angles the background increases by about 10% from that at low angles. As no satisfactory functional form for the background could be found, except the flat background already used, an arbitrary background of straight-line sections was subtracted in an attempt to get better agreement in the high-angle region (Rietveld, 1969). The  $R$  factor ( $= 0.17$ ) achieved with this refinement [(2) in Table 2], cannot be directly compared with that obtained when the background was not subtracted from the scan intensities [(1) in Table 2].

Table 1. Final parameters for the constrained refinement, for which  $R = 0.11$

	Parameter value	Standard deviation
Scale factor	305.7	2.3
Cell parameters	$a$ ( $\text{\AA}$ ) $\alpha$ ( $^\circ$ )	4.0629 0.006
Bond lengths ( $\text{\AA}$ )	O-C C-S	1.205 1.510
Overall isotropic temperature factor $B$ ( $\text{\AA}^2$ )	1.83	0.08
Flat background	3071.7	46.7
Zero error in $2\theta$ ( $^\circ$ )	-0.073	0.005
Peak-shape half-width parameters ( $\text{deg}^2$ )	$u$ $v$ $w$	2.81 -1.49 0.48
		0.23 0.18 0.03

Table 2. Comparison of gas phase and crystal diffraction results

Bond	O-C	C-S	Total length O-C-S	$R$ factor
Gas phase	1.16 (1) $\text{\AA}$	1.56 (1) $\text{\AA}$	2.72 (2) $\text{\AA}$	
Vegard (1931)	1.10	1.97	3.07	
Refinement (1)	1.21 (3)	1.51 (3)	2.72 (4)	0.11
Refinement (2)	1.19 (4)	1.54 (3)	2.73 (5)	0.17
Refinement (3)	1.14 (2)	1.47 (2)	2.61 (3)	0.12

(1) Flat background. (2) Arbitrary segmented background removed. (3) Sample position variable.

Although the agreement at high scattering angles was improved, the parameters of importance, namely the unit-cell and atomic positional parameters did not differ from those of refinement (1) by more than one standard deviation (based on  $N_e$  rather than  $N$ ). Consequently, despite the discrepancy at large scattering angles in refinement (1), the structural parameters do not appear to be very sensitive to the detailed form assumed for the observed background. The bond lengths for refinement (2) are given in Table 2.

It may also be noted that the difference plot shows small discrepancies between the positions of the calculated and observed diffraction peaks. These discrepancies persisted in refinement (2). The discrepancies are small and similar to those found in other neutron profile measurements. The variation of the discrepancy,  $\Delta = 2\theta_{\text{obs}} - 2\theta_{\text{calc}}$ , was analysed as a function of scattering angle and could be approximately described by a straight line of equation  $\Delta = 0.164 - 0.0032(2\theta)$  (degrees) giving  $\Delta = 0^\circ$  for  $2\theta \sim 51^\circ$ . This is close to the focusing angle ( $2\theta = 57.05^\circ$ ) for the spectrometer configuration and suggests that a systematic error is present. Another refinement, (3), was therefore made with the background subtracted as in refinement (2), but including new parameters to describe a possible misplacement of the sample on the spectrometer. This was done by adding two terms to the scattering-angle zero,  $2\theta_{\text{zero}}^{\text{calc}}$ , giving  $2\theta_{\text{zero}}^{\text{calc}} = P_5 - P_3 \cos 2\theta - P_4 \sin 2\theta$ , where  $P_5$  is the refinement variable corresponding to the scattering-angle zero error in the absence of mis-orientation. The new parameters,  $P_3$  and  $P_4$ , describe the possible shift of the sample parallel and perpendicular to the incident beam in the plane in which the measurements were made. The effect of this refinement was to decrease the  $R$  factor from 0.17 to 0.12, suggesting that the new parameters were statistically significant. However, the parameter values in the final cycle of refinement (3) implied that the scattering-angle zero error had increased to  $5.2(0.7)^\circ$  while the unit-cell side and the O—C bond

length decreased by  $\sim 1\%$  [(3) in Table 2]. Refinement (3) also suggested that the sample was misplaced on the spectrometer by  $75(10)$  mm. This 'shift' of the sample position and the new scattering-angle zero are inconsistent with the experimental conditions while the resulting changes in the bond length and unit cell also appear to be unreasonable. Consequently, misplacement of the sample does not seem to be the reason for the discrepancies. We are unable to suggest any other reasonable explanation.

### Conclusion

This analysis constitutes the first determination of the bond lengths in solid COS by elastic neutron scattering. They are found to be  $1.21(3)$  Å for the O—C distance and  $1.51(3)$  Å for the C—S distance. Those reported by Townes, Holden & Merritt (1948), using electron diffraction in the gaseous phase, were  $1.16(2)$  and  $1.56(2)$  Å respectively. Although the bond lengths in these analyses differ, it must be remembered that there is a high unavoidable correlation between the two bond-length parameters. The total molecular length is not affected in this way and we see that the gaseous-phase and solid-phase measurements both yield a value of  $2.72$  Å.

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### References

- PAWLEY, G. S. (1980). *J. Appl. Cryst.* **13**, 630–633.  
 RIETVELD, H. M. (1969). *J. Appl. Cryst.* **2**, 65–71.  
 SAKATA, M. & COOPER, M. J. (1979). *J. Appl. Cryst.* **12**, 554–563.  
 TOWNES, C. N., HOLDEN, A. H. & MERRITT, F. R. (1948). *Phys. Rev.* **74**, 113–1133.  
 VEGARD, L. (1931). *Strukturbericht*, **2**, 373.