

By electron diffraction and electron microscopy methods data were obtained on growth direction, symmetry and cell dimensions in the new monoclinic *ab*-projection, which are confirmed by the results found by X-ray techniques.

A Zeiss EM-9A 60 kV electron microscope has been used, with a selected area of about 1 μm in diameter. The grids were supported with a collodium film. The camera constant 2 λ L was externally calibrated with TlCl and also indirectly calibrated by the X-ray parameters of the SiAs sample.

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Revised Analysis of Molecular Vibrations of Sulphur Trioxide

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Three events have moved us to repeat the previous analysis¹ of molecular vibrations of sulphur trioxide: (i) the criticism by L. H. Jones,² who has questioned the correctness of some of our results, (ii) the appearance of an improved experimental value³ of ζ_3 for SO_3 , and (iii) an interesting study of AlCl_3 by Zasorin and Rambidi,⁴ which suggests that an analysis of mean amplitudes of SO_3 similar to the previous one,¹ but studying the quantities at high temperatures, might be valuable and interesting.

(i) We realize the correctness of Jones' results² and are thankful to him for having pointed out the errors in our previous calculations. According to our revised calculations the limits of accuracy (± 5 and $\pm 1 \text{ cm}^{-1}$) for ν_3^* and ν_4^* (in S^{18}O_3), as given in the last lines of the bottom paragraph on p. 1584 in the cited paper,¹ should be corrected to ± 0.5 and $\mp 0.2 \text{ cm}^{-1}$, respectively. This correction also changes some of the conclusions of the same paragraph, inasmuch as the revised calculations are well compatible with the statements of Duncan and Mills referred to in the paragraph.¹

(ii) A slight refinement of the force field for SO_3 was performed using the Coriolis constant of $\zeta_3 = 0.465 \pm 0.020$ from Milne and Ruoff³ along with $\nu_3 = 1391.3 \text{ cm}^{-1}$ from the same work, and otherwise the same spectral data as previously.¹ The derived force constants in the E' species, viz. (in $\text{mdyne}/\text{\AA}$)

$$F_1 = 10.58 \mp 0.10, F_{12} = -0.34_6 \pm 0.06_3,$$

$$F_2 = 0.621 \pm 0.002 \quad (1)$$

are very similar to those recently published by Ruoff.⁵

The present force constants were used to calculate the mean amplitudes of vibration and shrinkage effect in sulphur trioxide at several temperatures with the results given in Table 1.

Table 1. Mean amplitudes of vibration and shrinkage effect (\AA units) for sulphur trioxide: $^{32}\text{S}^{16}\text{O}_3$.

T [$^{\circ}\text{K}$]	$u(\text{S}-\text{O})$	$u(\text{O}\cdots\text{O})$	δ
0	0.0348	0.0514	0.0020
298	0.0349	0.0538	0.0023
500	0.0358	0.0596	0.0031
1000	0.0409	0.0760	0.0055
1500	0.0471	0.0909	0.0080
2000	0.0530	0.1041	0.0106

(iii) Zazorin and Rambidi⁴ in an interesting work have used mean amplitudes of vibration and shrinkage effect from electron diffraction at 800°K as part of the data to determine some of the vibrational frequencies in AlCl_3 . According to a closer examination⁶ it seems that the success of these workers⁴ is conditional on the relatively high temperature of their experiment. In a part of the previous analysis¹ of SO_3 emphasis is laid on the required limits of error for u_{OO} , *i.e.* the precision which would make the quantity useful in accurate determinations of force constants. In view of the analyses of aluminum trichloride^{4,6} it seems to be of interest to investigate the effect of temperature also on these error limits. Table 2 gives a detailed account of the calculated results for u_{OO} at the different temperatures. Δu indicates approximately the required precision for this quantity in order to make it fix the force constants within error limits as given in (1). At room temperature the limits of error for u_{OO} should be $\pm 0.0001_5$ \AA (rather than ± 0.0003 \AA as stated in the previous article¹). The interesting point is to notice how the required limits of error increase with increasing temperature; they are for instance approximately doubled from room temperature to 1000°K . Still the precisions of electron-diffraction experiments today are not good enough to give as narrow limits of error as the listed ones in Table 2. But it should be remembered that the basis of the present calculations (± 0.02 for ζ_3 and about ± 0.06 mdyne/ \AA

Table 2. Calculated results for $u(\text{O}\cdots\text{O})$ (\AA units) in $^{32}\text{S}^{16}\text{O}_3$ at different temperatures from ζ_3 with the error limits included.

ζ_3	0.485	0.465	0.445	
F_{12}	0.283	0.346	0.409	
[mdyne/ \AA]				
u_{OO} at				
T [$^{\circ}\text{K}$]			$\pm \Delta u$	
0	0.0515	0.0514	0.0513	$\pm 0.0001_2$
298	0.0540	0.0538	0.0537	$\pm 0.0001_5$
500	0.0598	0.0596	0.0594	$\pm 0.0001_9$
1000	0.0763	0.0760	0.0758	$\pm 0.0002_9$
1500	0.0913	0.0909	0.0906	$\pm 0.0003_7$
2000	0.1045	0.1041	0.1037	$\pm 0.0004_3$

for F_{12}) represents a relatively large accuracy; in another analysis of the same kind⁷ the required error limits were taken larger by a factor of two or three. Thus it may be concluded with some reservations that the required error limits for mean amplitudes to be used in relatively accurate determinations of force constants tend to approach accessible magnitudes when the temperature is increased. It is also interesting to notice that the required error limits for the shrinkage effect are highly dependent on temperature, but are still far from attainable by electron diffraction (*e.g.* ∓ 0.00004 \AA at 1000°K as the required precision on the basis of the present analysis).

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