

Molecular Vibrations of Sulphur Trioxide

Accurate Determination of Harmonic Force Field, and Calculated Mean Amplitudes and Shrinkage Effect

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Spectroscopic calculations were performed for sulphur trioxide, using recent spectral data from Krakow and Lord, who furnished one Coriolis constant (ζ) in addition to reinvestigated fundamental frequencies. The applicability of the observed ζ value for an accurate force field determination was demonstrated, following the technique of I.M. Mills. Also the possibility of using mean amplitudes of vibration or the Bastiansen-Morino shrinkage effect was investigated, but the ζ constant was found to be the most superior quantity for the mentioned purpose. The required accuracy for mean amplitudes and the shrinkage effect was estimated to be undoubtedly higher than one could hope to achieve by gaseous electron diffraction to-day.

Using the best harmonic force field which one could derive, the mean amplitudes of vibration and shrinkage effects at various temperatures were computed. Finally, one performed some considerations for the isotopically substituted compound with ^{18}O .

ASSIGNMENT OF FUNDAMENTALS

The structure of sulphur trioxide is generally accepted to be that of a planar symmetrical XY_3 model of D_{3h} symmetry.

Until quite recently the assignment of fundamental frequencies for sulphur trioxide has been rather controversial. Below we give the assignments from Landolt-Börnstein's compilation of 1951, along with more recent investigations (frequencies in cm^{-1}).

	$\nu_1(A_1')$	$\nu_2(A_2'')$	$\nu_3(E')$	$\nu_4(E')$
Landolt-Börnstein ¹	1068	530	1390	653
Khachkuruzov ²	1069	652	1333	440
Lovejoy <i>et al.</i> ³	—	495	1391	529
Krakow <i>et al.</i> ⁴	—	498	1391.1	531

The early assignment¹ was used by Venkateswarlu *et al.*⁵ and Pistorius⁶ in their force constant calculations. The Urey-Bradley force constants of Janz *et al.*⁷ are based on a still earlier assignment. The assignment of Khachkuruzov² was used in the computations of Nagarajan *et al.*⁸⁻¹⁰ which also contain mean amplitudes of vibration and shrinkage effect. Mean amplitudes of vibration for SO₃ have also been calculated by Srinivasacharya *et al.*,¹¹ who, however, applied the Landolt-Börnstein assignment. Cyvin *et al.*¹² in their studies of mass-dependence of Coriolis constants favoured the Khachkuruzov² assignment rather than that of Landolt-Börnstein.¹

The controversy as to the correct assignment of the SO₃ fundamentals seems now to be resolved through the infrared works of Lovejoy *et al.*³ and Krakow and Lord.⁴ Especially in the latter work⁴ the investigators were able to study the fine structure of the ν_3 band, and they deduced the Coriolis constant of $\zeta_3 = 0.48$.

DETERMINATION OF THE HARMONIC FORCE FIELD

In a planar symmetrical XY₃ molecule one piece of information is needed in addition to the four frequencies in order to determine completely the harmonic field. The application of ζ constants for this purpose has been developed and strongly advocated by Mills *et al.*¹³⁻¹⁷ and Duncan.¹⁸ The method has been adopted by several investigators; one may especially mention Levin *et al.*¹⁹⁻²¹ As a matter of fact also Krakow and Lord⁴ used their observed ζ value (see above) to establish the force field. We have adopted their results with minor adjustments as the best values of force constants for sulphur trioxide:

$$F(A_1') = 10.768; F(A_2'') = 0.312$$

$$F_1(E') = 10.520; F_{12}(E') = -0.297; F_2(E') = 0.623;$$

all values in mdyne/Å. We have also adopted $R = 1.43$ Å as the equilibrium S—O distance.²²

DISCUSSION OF FORCE-FIELD DETERMINATIONS

The observed value of $\zeta_3 = 0.48$ (see above) was found to be very well useful for an accurate determination of the force-field. This feature confirms the general conclusions of Mills *et al.*¹³⁻¹⁶ It was intended to make a more detailed study of this problem; we therefore produced in the usual way¹⁶⁻²¹ the curves representing various calculated quantities as functions of interaction force-constant $F_{12}(E')$, taken over the whole range being compatible with real solutions. The curves for $F_1(E')$ and $F_2(E')$ are parts of the familiar force-constant ellipses; *cf.* Fig. 1 (a). In the same figure the calculated ζ_3 values

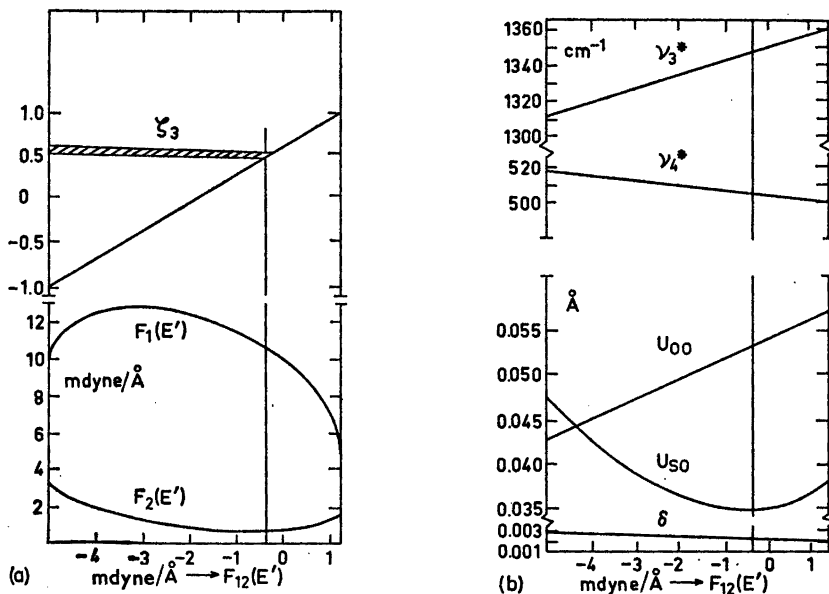


Fig. 1. Curves for certain quantities as functions of the $F_{12}(E')$ force constants:

- (a) $F_1(E')$ = stretching force constant of species E' ,
 $F_2(E')$ = bending force constant of species E' ,
 ζ_3 = Coriolis constant of $E' \times E'$ (z) type.
- (b) δ = Bastiansen-Morino shrinkage effect for $S^{16}O_3$ at 298°K,
 u_{SO} = mean amplitude of vibration for the bonded distance in $S^{16}O_3$ at 298°K,
 u_{OO} = mean amplitude of vibration for the non-bonded distance at 298°K,
 ν_3^* = stretching E' frequency in $S^{16}O_3$,
 ν_4^* = bending E' frequency in $S^{16}O_3$.

were plotted; the corresponding curve displays a large variation (from -1 to $+1$) through the considered range. Unfortunately, Krakow and Lord⁴ did not specify the error limits for their observed ζ_3 . If we take ± 0.02 as a reasonable (maybe somewhat too optimistic) estimate, we find the corresponding precision of F_{12} to be about ± 0.06 mdyne/Å, and also the F_1 and F_2 force-constants are fixed within narrow limits.

Theoretically, either of the two mean amplitudes of vibration (u) or the Bastiansen-Morino shrinkage effect (δ) might also be used to fix the force constants of the considered molecule as an alternative to the above described method. As a matter of fact, values of u obtained from gaseous electron diffraction have tentatively been used for this purpose in several instances.²³⁻³¹ In spite of this voluminous material, however, it is felt that still much more can be done as to a systematic investigation of this procedure and the inherent error limits. It was intended to use the present example of SO_3 to provide a contribution in this direction. Therefore we produced the curves of mean amplitudes and shrinkage effects as shown in Fig. 1 (b) and being analogous to the ζ curve discussed above. As an outcome of the diagram it must be

realized that the situation is not at all promising. If one should use the mean amplitude for the non-bonded distance (u_{OO}) to fix F_{12} within the limits of ± 0.06 mdyne/Å as above, the u value would have to be available with a precision of about ± 0.0003 Å. This is about one tenth of the actual error limits expected from modern gaseous electron diffraction to-day. The u value for the bonded (SO) distance might probably be observed with somewhat greater precision than u for the non-bonded (OO) distance. However, as seen from Fig. 1 (b) the requirements for u_{SO} are significantly larger than those for u_{OO} discussed above. This particularly unfavourable situation is due to a minimum of the u_{SO} curve in the vicinity of the actual range. Finally the shrinkage effect, which is a non-linear type,³² is very small and shows little variation throughout the whole range; cf. Fig. 1 (b).

From the point of view of spectroscopic calculations, on the other hand, very favourable conclusions are drawn from the above considerations connected to Fig. 1 (b). It is clear that the calculated values of u and the shrinkage effect may be quite reliable, even if the F_{12} force constant is not accurately fixed.

We have also made some considerations concerning the isotope effect on vibrational frequencies. Fig. 1 (b) includes the curves of $\nu_3^*(E')$ and $\nu_4^*(E')$ for the $S^{18}O_3$ compound, as calculated from the same force constants as used in the above computations. Duncan and Mills^{17,18} have articulated a warning against using observed frequencies of isotopic molecules as additional data for force-constant determinations. We appreciate their views, which have proved to be very stimulating for modern spectroscopic investigations. However, their general conclusions seem to be contradicted to some extent by the present example. Specifically one finds that the F_{12} constant could be fixed within ± 0.06 mdyne/Å if one could measure ν_3^* (for $S^{18}O_3$) with an accuracy of about ± 5 cm^{-1} , or ν_4^* with about ± 1 cm^{-1} . Such measurements, although not presently available, seem not at all to be unrealistic.

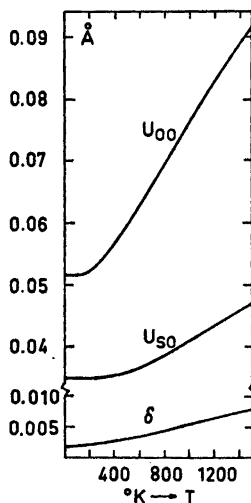


Fig. 2. Mean amplitudes of vibration (u) for bonded (SO) and non-bonded (OO) distances, and the Bastiansen-Morino shrinkage effect (δ) vs. temperature.

MEAN AMPLITUDES OF VIBRATION,
SHRINKAGE EFFECT, AND CORIOLIS CONSTANTS

The mean amplitudes of vibration and Bastiansen-Morino shrinkage effects, both for $S^{16}O_3$ and $S^{18}O_3$, were calculated using the force constants reported above. The results at the temperatures of absolute zero and 298°K are shown

Table 1. Mean amplitudes of vibration (u) and shrinkage effects (δ) in Å units for sulphur trioxide molecules.

Quantity	Temp. (°K)	$S^{16}O_3$	$S^{18}O_3$
u_{SO}	0	0.0348	0.0341
	298	0.0349 ± 0.0001	0.0342
u_{OO}	0	0.0515	0.0500
	298	0.0539 ± 0.0005	0.0528
δ	0	0.0020	0.0019
	298	0.0023	0.0023

in Table 1. Fig. 2 shows the same quantities (for $S^{16}O_3$) as functions of temperature, extended to 1500°K. The temperature dependence is seen to be greatest for the u_{OO} , and smallest for the shrinkage. The error limits reported in Table 1 for the u value at 298°K correspond to about ± 0.10 mdyne/Å for F_{12} . These limits have been taken larger than ± 0.06 mdyne/Å referred to above, because the above discussions (and Fig. 1) do not take into consideration the uncertainties in observed fundamentals, which were taken as the $S^{16}O_3$ frequencies.

Table 2. Vibrational frequencies (in cm^{-1}) and Coriolis constants for sulphur trioxide molecules.

Quantity	$S^{16}O_3$	$S^{18}O_3$
$\nu_1(A_1')$	1069 ^a	1007.7
$\nu_2(A_2'')$	498 ^a	486.8
$\nu_3(E')$	1391.1 ^a	1347.4
$\nu_4(E')$	531	505.1
$ \zeta_{23} (x,y)$	0.860	0.871
$ \zeta_{24} (x,y)$	0.510	0.492
$\zeta_3(z)$	0.480 ^a	0.516
$\zeta_4(z)$	-0.480	-0.516
$\zeta_{34}(z)$	0.877	0.857

^a Observed quantity used in the calculations.

Table 2 shows the calculated frequencies and complete sets of Coriolis constants for the considered molecules. Notice the relations:

$$\zeta_{23}^2 + \zeta_{24}^2 = 1; \quad \zeta_3 + \zeta_4 = 0; \quad \zeta_3 \cdot \zeta_4 - \zeta_{34}^2 = -1$$

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