Vibrational Frequency Isotope Shifts for SO_3*

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Stølevik *et al.*[1] have recently determined the harmonic force constants of SO_3 from the vibrational frequencies and Coriolis constants of the normal species. In this paper [1] they have included some calculations of frequencies of $S^{18}O_3$ and have stated that "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}." These limits seem very generous compared to other systems; however, I have been assured [2] that they are not typographical errors. If these limits are indeed correct, the observation of the vibrational frequencies of $S^{18}O_3$ would be extremely useful for estimation of the force constants. Therefore, I have made calculations of the frequencies of $^{32}S^{18}O_3$, $^{34}S^{16}O_3$, and $^{34}S^{18}O_3$ in which F_{12} (E') is varied and $F_1(E')$ and $F_2(E')$ are chosen to fit the E' frequencies of the normal species. The results are presented in Table 1.

From these results it is apparent that to determine F_{12} to ± 0.06 mdyne/Å one must measure ν_3* (for $S^{18}O_3$) with an accuracy of about ± 0.4 cm^{-1} or ν_4* with an accuracy of ± 0.2 cm^{-1} rather than ± 5 cm^{-1} and ± 1 cm^{-1}, respectively. Actually it is the isotope shift, $\nu_3(^{32}S^{16}O_3) - \nu_3{}^*(^{32}S^{18}O_3)$, which must be determined to ± 0.4 cm^{-1}. Even this is not unrealistic, especially if extremely sharp lines can be obtained for a dispersion in an argon matrix at very low temperatures.

As Table 1 shows, even more useful would be the difference $\nu_3(^{34}S^{16}O_3) - \nu_3(^{32}S^{18}O_3)$ which would only have to be known to ± 0.7 cm^{-1} to fix $F_{12}(E')$ to ± 0.06 mdyne/Å.

Perhaps it should be mentioned that a knowledge of anharmonicity corrections would be necessary for determining the true harmonic force constants, though the results on the observed frequencies should be fairly good for this molecule.

Table 1. E' Symmetry force constants of SO_3.

F_{12} [a]		−0.097	−0.297 [b]	−0.497
F_1		10.1707	10.5061	10.8119
F_2		0.6357	0.6229	0.6119
$^{32}S^{16}O_3$	ν_3 [c]	1391.1	1391.1	1391.1
	ν_4	531.0	531.0	531.0
$^{32}S^{18}O_3$	ν_3	1349.0	1347.5	1346.0
	ν_4	504.6	505.1	505.7
$^{34}S^{16}O_3$	ν_3	1372.1	1372.9	1373.6
	ν_4	528.8	528.5	528.2
$^{34}S^{18}O_3$	ν_3	1329.2	1328.5	1327.8
	ν_4	502.5	502.8	503.1
$\nu_3(^{34}S^{16}O_3) - \nu_3(^{32}S^{18}O_3)$		23.1	25.4	27.6

[a] Units of F_i are millidynes per Ångström.
[b] This is close to the solution which fits the Coriolis constant, ζ_3.[1]
[c] Units of ν_i are cm^{-1}.

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1. Stølevik, R., Andersen, B., Cyvin, S. J. and Brunvoll, J. *Acta Chem. Scand.* **21** (1967) 1581.
2. Cyvin, S. J. *Private communication.*

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On the Hybridization in the S_N2 Mechanism in Nucleophilic Displacement of Carbon

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Several concepts in chemistry, such as bond direction and bond angle, have been explained conceptually in a simple way by means of models based on concepts from quantum chemistry (such as sym-