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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On the Hybridization in the $S_N 2$ 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-

metry and other properties of atomic and molecular wave functions, overlap, *etc.*). The interpretation of the bond properties of the carbon atom in organic molecules by means of hybridization of s and p orbitals is perhaps the most successful and well known case. However, conventional hybridization has several shortcomings, some of which can be removed by applying so called complex hybridization.[1-3] The essential difference between these two hybridization models is, that in conventional hybridization hybrid direction and bond direction are identical and the unitary hybridization matrix is real; in the complex model the bond direction is defined as the direction to the gravity centre of the hybrid density function, the unitary hybridization matrix is permitted to have complex elements and all the four hybrids are supposed to be equivalent as to their content of s orbital. In this note we will compare these two models when applied to the nucleophilic displacement reaction on carbon.

The reaction mechanism termed S_N2 is a bimolecular, nucleophilic substitution reaction. It is characterized by a one-step attack by a nucleophilic reagent X which displaces the group Y attached to the carbon atom (Fig. 1). An important
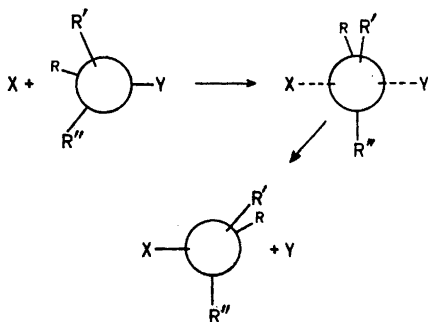

Fig. 1.

character of this mechanism is that it generally leads to an inversion of the steric configuration. This is interpreted so that the attack by the nucleophilic reagent X takes place on the side of the flattened structure opposite to the group Y which has to be released.

Conceptually it is of interest to look at this flattened structure. From hybridiza-

tion point of view it may be considered as a limit case of the tetrahedral (sp^3) configuration, which has been deformed so, that the three bonds to R, R′, and R″ are in a plane perpendicular to the reaction coordinate. For simplicity we assume that the structure is symmetrical as regards the bond angles between these three bonds and with the bond to R′ coinciding with the z axis. The deformation is then symmetrical about the reaction coordinate and is described by only one bond angle variable (in the limit case it is 90°; see Fig. 2).
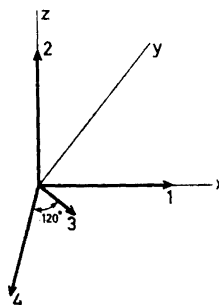

Fig. 2.

In the tetrahedral case the hybrid of the carbon atom at the center A in the direction of the x axis is given by

$$h_A = \tfrac{1}{2}s + (\sqrt{3/2})p_x$$

where s and p are the orthonormal atomic orbitals of carbon. This hybrid is the same in both models.

In conventional hybridization the deformation will change this hybrid into one with no content of s orbital, or simply

$$h_A{}' = p_x$$

which enters into the bond formation as a p_o orbital.

In complex hybridization with all four hybrids equivalent as to their s orbital content, the hybrid for the appropriate limit case is

$$h_A{}'' = \tfrac{1}{2}s + i(\sqrt{3/2})p_x$$

As was pointed out above, in both cases the hybridization matrix is supposed to be unitary, *i.e.* the hybrids are normalized and orthogonal for each center.

A simple but approximative way of comparing the bonding properties of these hybrids is to use the overlap as a measure

Table 1. The overlap S_{AB} between some combinations of hybrids, of which h_A represents the proper hybrid of the planar structure (h_A' in conventional hybridization; h_A'' in complex hybridization).

h_B	$h_A' = 2p_x$	$h_A'' = \frac{1}{2}\, 2s + i(\sqrt{3}/2)\, 2p_x$
$1s$	$(1s|2p_\sigma)$	$\frac{1}{2}\,(1s|2s)$
$\frac{1}{2}\, 2s + (\sqrt{3}/2)\, 2p_x = h_A'$ $2p_x = h_A'$	$\frac{1}{2}\,(2s|2p_\sigma) + (\sqrt{3}/2)\,(2p_\sigma|2p_\sigma)$ $(2p_\sigma|2p_\sigma)$	$\frac{1}{4}\,(2s|2s) + (\sqrt{3}/4)(2s|2p_\sigma)$
$\frac{1}{2}\, 2s + i(\sqrt{3}/2)\, 2p_x =$ $= h_A''$		$\frac{1}{4}\,(2s|2s) + (\sqrt{3}/4)\,(2p_\sigma|2p_\sigma)$

of the bond strength. Since we have to deal also with hybrids with complex coefficients, we will define the bonding overlap between two hybrids of centers A and B as

$$S_{AB} = \tfrac{1}{2}\{(h_A|h_B) + (h_B|h_A)\}$$

which is a real quantity. h_B is the appropriate bonding hybrid of center B corresponding to the bonding atom of the substituent Y in Fig. 1.

In conventional hybridization the hybrid in the limit case will contribute to the bonding as a p_σ orbital overlapping the proper real hybrid of center B. In complex hybridization the situation is another, and the hybrid will always contribute with half the s orbital to the overlap, whereas the p orbital in the limit state has an imaginary coefficient and will contribute only if the hybrid of center B is complex. In Table 1 the overlap expressions are given for the planar limit state, represented by h_A' and h_A'' for the conventional and complex models, respectively. For h_B are listed the $1s$ function and the ordinary sp^3 hybrid. The two last rows in the table refer to the case when the structure at atom B is flattened.

At ordinary bond length and increasing distance between the centers the overlap is definitely lower in the complex model than in the conventional one, when h_B is an s orbital or an ordinary sp^3 hybrid. The factor $\tfrac{1}{2}$ is sufficient to ensure that so is the case at interatomic distances equal or close to the ordinary bond length; at greater distances already the integrals themselves are smaller, since a p_σ function in the integrals causes them to decrease more slowly than a corresponding s function. In the last case with two planar structures, the overlap is almost the same (within two decimals) at the ordinary

bond length, but at longer interatomic distances the overlap will decrease somewhat slower in the complex model. However, this structure with planar conformations at centers A and B simultaneously is not realistic; a slight deformation at B opposite to that at A would perhaps rather be expected.

As to numerical values,[5] the overlap of an ordinary $sp^3 - sp^3$ carbon-carbon bond ($R = 1.54$ Å) is 0.65. When one of these configurations is flattened (with no change in R), the overlap decreases to 0.47 in conventional hybridization and to 0.24 in complex hybridization. In the latter case the overlap is decreased to a value comparable to that of the overlap of an ordinary, aromatic π bond.

From this follows that the complex hybridization seems to work well in the angular interval which is covered by conventional hybridization.

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