Vibrational Frequency Isotope Shifts for SO$_3$^

LLEWELLYN H. JONES

Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico 87544, U.S.A.

Stelevik 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$^{34}$O$_3$ and have stated that “one finds that the $F_{12}$ constant could be fixed within $\pm 0.06$ mdyn/Å if one could measure $v_2^*$ (for S$^{34}$O$_3$) with an accuracy of about $\pm 0.4$ cm$^{-1}$, or $v_4^*$ with about $\pm 1$ 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$^{34}$O$_3$ would be extremely useful for estimation of the force constants. Therefore, I have made calculations of the frequencies of S$^{34}$O$_3$, S$^{32}$O$_3$, and S$^{33}$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 $\pm 0.06$ mdyn/Å one must measure $v_2^*$ (for S$^{34}$O$_3$) with an accuracy of about $\pm 0.4$ cm$^{-1}$ or $v_4^*$ with an accuracy of $\pm 0.2$ cm$^{-1}$ rather than $\pm 5$ cm$^{-1}$ and $\pm 1$ cm$^{-1}$, respectively. Actually it is the isotope shift, $v_2(S^{34}O_3) - v_2(S^{33}O_3)$, which must be determined to $\pm 0.4$ 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 $v_2(S^{34}O_3) - v_2(S^{33}O_3)$ which would only have to be known to $\pm 0.7$ cm$^{-1}$ to fix $F_{12}(E')$ to $\pm 0.06$ mdyn/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.


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On the Hybridization in the $S_2$ 2 Mechanism in Nucleophilic Displacement of Carbon

OLLE MARTENSSON

Quantum Chemistry Group, Uppsala University, Box 518, S-751 20 Uppsala 1, Sweden

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-

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Table 1. $E'$ Symmetry force constants of SO$_3$:

<table>
<thead>
<tr>
<th></th>
<th>$F_{12}$</th>
<th>$F_1$</th>
<th>$F_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{32}$S$^{16}$O$_3$</td>
<td>1391.1</td>
<td>1391.1</td>
<td>1391.1</td>
</tr>
<tr>
<td>$^{34}$S$^{16}$O$_3$</td>
<td>1349.0</td>
<td>1347.5</td>
<td>1346.0</td>
</tr>
<tr>
<td>$^{33}$S$^{18}$O$_3$</td>
<td>1372.1</td>
<td>1372.9</td>
<td>1373.6</td>
</tr>
<tr>
<td>$^{34}$S$^{18}$O$_3$</td>
<td>1329.2</td>
<td>1328.5</td>
<td>1327.8</td>
</tr>
<tr>
<td>$^{34}$S$^{16}$O$_3$</td>
<td>23.1</td>
<td>25.4</td>
<td>27.6</td>
</tr>
</tbody>
</table>

$^a$ Units of $F_1$ are millidynes per Ångström.

$^b$ This is close to the solution which fits the Coriolis constant, $\zeta_2$.

$^c$ Units of $v_2$ are cm$^{-1}$.

$^*$ This work done under the auspices of the U.S. Atomic Energy Commission.

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