Mean Amplitudes of Vibration and Shrinkage Effects of Hexafluorobenzene

D. FREMSTAD, J. BRUNVOLL and S. J. CYVIN

Institutt for teoretisk kjemi, Norges tekniske høgskole, Trondheim, Norway

Approximate mean amplitudes of vibration\(^1\) and Bastiansen-Morino shrinkage effects\(^2\) have been obtained for hexafluorobenzene. The computations were performed by a series of GIER-ALGOL programs.\(^3\)

Preliminary calculations. Force constants were roughly estimated following the idea of Steele and Whiffin (Ref.\(^4\), especially Table 3 therein) with transferring most of the force constants from benzene. The set of benzene force constants has presently been obtained from data of Brooks et al.\(^4\). The calculated frequencies were not too bad as compared to the experimental values of Steele and Whiffin.\(^4\) The discrepancies are comparable to those of Table 3 of the cited work.

Refined calculations. A final set of force constants was produced from the L matrix of the preliminary calculations, along with the experimental frequencies.\(^4\) Thus the force constants were adjusted to fit accurately the frequencies. Hence the new set of force constants is probably (but not necessarily) an improvement of the preliminary set.

The mean amplitudes of vibration and shrinkage effects obtained from these calculations are given in Tables 1 and 2, respectively.

| Table 2. Bastiansen-Morino shrinkage effects* in hexafluorobenzene (Å units). |
|-----------------|--------|--------|--------|
|                  | \(T = 0\) | 298°K  | 373°K  |
| C\(_1\), C\(_2\) | 0.0029  | 0.0033 | 0.0036 |
| C\(_1\), C\(_4\) | 0.0039  | 0.0046 | 0.0050 |
| C\(_1\), F\(_1\) | 0.0034  | 0.0042 | 0.0046 |
| C\(_2\), C\(_3\) | 0.0069  | 0.0098 | 0.0101 |
| C\(_4\), F\(_2\) | 0.0082  | 0.0110 | 0.0124 |
| F\(_1\), F\(_1\) | 0.0047  | 0.0058 | 0.0065 |
| F\(_2\), F\(_2\) | 0.0104  | 0.0145 | 0.0165 |
| F\(_3\), F\(_3\) | 0.0126  | 0.0181 | 0.0208 |

*These are the “practical” shrinkage effects. For a precise definition of the quantities see Cyvin, S. J. Acta Chem. Scand. 17 (1963) 296.

Suggestion for other refinements. In the preliminary set the force constants were at once adjusted accurately to the frequencies of Species \(A_{1g}\). A similar procedure could be extended to the other species to give more reliable force constants than the presently calculated. It seems, however, not worth while performing such refinements at present for several reasons: (a) Uncertainties in the assignment of the frequencies. (b) Comparatively small effects on the results, as was verified by the present calculations. (c) The desired accuracy is not large for the present purpose of comparing the results with those from electron-diffraction. (d) The present method was more convenient for machine solution.

References:

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Vibration of Polyatomic Molecules (Report),
Norges tekniske høgskole, Trondheim 1964.
Chem. Scand. 16 (1962) 820; Brooks, W.
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Behaviour of Secretin, Cholecysto-
kinin and Pancreozymin to Oxida-
tion with Hydrogen Peroxide

VIKTOR MOTT

Department of Chemistry II, Karolinska
Institutet, Stockholm 60, Sweden

It is known from the work of Dedman,
Farmer and Morris that the pituitary
adrenocorticotropic hormone may be inac-
tivated by treatment with hydrogen peroxide and the activity restored on
reduction, preferably with cysteine. The
inactivation is accompanied by the oxida-
tion of the methionine residue of the
hormone to the corresponding sulphonides. An essentially similar behaviour is exhibited by the α- and β-melanocyte stimulating
hormones, and by the parathyroid
hormone.

In work towards the isolation of the
gastrointestinal hormones secretin, chole-
cystokinin and pancreozymin it has been
pointed out by Jorpes and Mutt that
during the purification procedure it has
been easy to separate secretin from chole-
cystokinin and pancreozymin but that
the latter two activities have gone parallel
in the various purification steps. This was
the case in 1958 when we reported on a
preparation with 22 Ily cholecystokinin
units and 120 Crick, Harper and Raper
pancreozymin units per mg and it has
been true of later work where some one
hundred times purer material has been obtained. Our purest preparations to
date still contain methionine, which is
absent from secretin. Consequently it
seemed to be of interest to determine
whether the cholecystokinin and pancreo-
yzin activities would both be affected
by mild oxidation with hydrogen perox-
ide, whether an eventual inactivation
would be reversible, and whether secretin,
as could be anticipated from the amino
cacid composition, would exhibit a greater
stability to hydrogen peroxide.

It was found in the experiments
described below that under conditions of
oxidation where secretin loses no ac-
tivity cholecystokinin is inactivated to
the extent of at least 98%. This inacti-
vation may be largely reversed by treat-
ment of the inactivated material with
cysteine. Pancreozymin behaves in this
respect like cholecystokinin, although
because of the difficult assay methods
minor differences in extent of inactivation
and reactivation are not excluded by the
present investigation.

Table 1. Biological activity of hydrogen peroxide treated secretin, cholecystokinin-pancreozymin, and of the oxidized cholecystokinin-pancreozymin after reactivation with cysteine.

<table>
<thead>
<tr>
<th>Material</th>
<th>Activity, % of initial</th>
</tr>
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<tbody>
<tr>
<td>H₂O₂-treated secretin</td>
<td>ca. 100</td>
</tr>
<tr>
<td>H₂O₂-treated cholecystokinin-pancreozymin</td>
<td>cholecystokinin: &lt; 2</td>
</tr>
<tr>
<td></td>
<td>pancreozymin: &lt; 2</td>
</tr>
<tr>
<td>H₂O₂-treated cholecystokin-pancreozymin after reactivation with cysteine</td>
<td>cholecystokinin: ca. 90</td>
</tr>
<tr>
<td></td>
<td>pancreozymin: ca. 90</td>
</tr>
</tbody>
</table>

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