Rotation-internal rotation theory and its application to the phenol molecule

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Rotation-Internal Rotation Theory
and its Application to the Phenol Molecule

ABHANDLUNG
zur Erlangung der Würde eines Doktors der Naturwissenschaften
der EIDGENÖSSISCHEN TECHNISCHEN HOCHSCHULE ZÜRICH

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From equations (4.2), (4.8) and (4.9) it follows that $C_2 (j, \varphi)$ is a symmetry operation of the Hamiltonian if

$$a^{(k)}_{ij} = 0 \text{ for } k = 1, 2 \text{ and } i \neq j \text{ (i, j = 1, 2, 3)}$$

$$\varphi = -\tau \text{ for } j = 1, 2 \text{ and } \varphi = \tau \text{ for } j = 3$$  \hspace{1cm} (4.25)

The relation $a^{(k)}_{rs} = a^{(k)}_{sr}$ is evident from equations (4.5) and (4.8). In the following considerations, $k$ takes always the values 1 and 2.

(i) The symmetry operation $C_2 (1, -\tau)$:

$C_2 (1, -\tau)$ is a symmetry operation of the Hamiltonian if (c. f. (4.25))

$$a^{(k)}_{12} = a^{(k)}_{13} = 0$$  \hspace{1cm} (4.26)
According to (4.8), this condition means that

\[
A_{12}^{(k)} = A_{13}^{(k)} = 0 \quad \text{and} \quad r_k = 0 \text{ or } d = 0
\]

To guarantee that \( A_{12}^{(k)} \) and \( A_{13}^{(k)} \) vanish, the two parts of the semi-rigid body must have a plane of symmetry \( \sigma_v^1 \) at \( \tau = 0 \); but \( \sigma_v^1 \) involves also that the two \( r_k \) vanish.

Result: \( \sigma_v^1 \) generates \( C_2(1, -\tau) \) if it is a plane of symmetry for both \( A^{(1)} \) and \( A^{(2)} \).

(ii) The symmetry operation \( C_2(2, -\tau) \):

According to (4.25), \( C_2(2, -\tau) \) is a symmetry operation of the Hamiltonian if

\[
a_{12}^{(k)} = a_{23}^{(k)} = 0
\]

For this, the two parts of the semi-rigid body must have a plane of symmetry \( \sigma_v^2 \) at \( \tau = 0 \) (c. f. (4.8)).

Result: \( \sigma_v^2 \) generates \( C_2(2, -\tau) \) if it is a plane of symmetry for both \( A^{(1)} \) and \( A^{(2)} \).

(iii) The symmetry operation \( C_2(3, \tau) \):

According to (4.25), \( C_2(3, \tau) \) is a symmetry operation of the Hamiltonian if

\[
a_{13}^{(k)} = a_{23}^{(k)} = 0
\]

This means that \( A_{13}^{(k)} = A_{23}^{(k)} = 0 \) and \( r_k = 0 \) or \( d = 0 \). \( A_{13}^{(k)} \) and \( A_{23}^{(k)} \) vanish if \( A^{(1)} \) and \( A^{(2)} \) both have a symmetry plane \( \sigma_h^1 \). We denote by \( \sigma_h^{(k)} \) the symmetry plane of \( A^{(k)} \).

If \( \sigma_h^{(1)} = \sigma_h^{(2)} \), it follows that \( d = 0 \).

If \( \sigma_h^{(1)} \neq \sigma_h^{(2)} \), \( d \) does not vanish and we need the additional condition that \( r_1 = r_2 = 0 \).
\[ r_1 = r_2 = 0 \quad \text{if } A^{(1)} \text{ and } A^{(2)} \text{ both have a symmetry plane } \sigma_v \]

or a pure rotational symmetry \( C^{(k)}_m \) around the internal rotation axis with \( m > 1 \). 

Result: \( C_2(3, \tau) \) is a symmetry operation of the Hamiltonian if both parts of the semi-rigid body (without the mass points on the internal rotation axis) have a common plane of symmetry \( \sigma_h \) or different symmetry planes \( \sigma^{(1)}_h \) and \( \sigma^{(2)}_h \) with the additional condition (4.27).

We denote by \( C_{s1} \) the group of order 2 with the elements \( E \) (unity) and \( C_2(i, \varphi) \) and by \( C_1 \) the trivial group of order 1. We get the following possibilities for the subgroup \( F \) of \( G(M) \):

\[
\begin{align*}
F &= C_1 : \text{ no symmetry } C_s \\
F &= C_{s1} : \text{ symmetry plane } \sigma_v \text{ for } A^{(1)} \text{ and } A^{(2)} \\
F &= C_{s2} : \text{ symmetry plane } \sigma_v \text{ for } A^{(1)} \text{ and } A^{(2)} \\
F &= C_{s3} : \text{ symmetry plane } \sigma_h \text{ for } A^{(1)} \text{ and } A^{(2)} \text{ or } \\
& \quad \sigma^{(1)}_h \text{ for } A^{(1)} \text{ and } \sigma^{(2)}_h \text{ for } A^{(2)} \text{ together with condition (4.27)} \\
F &= V : \text{ symmetries mentioned above of two of the three groups } \\
& \quad C_{s1}, C_{s2}, C_{s3}, \text{ since } V = C_{s1} \cdot C_{s2} = C_{s2} \cdot C_{s3} = C_{s3} \cdot C_{s1} \\
& \quad (c. f. table 16) \\
& \quad C_{s1}, C_{s2} \text{ and } C_{s3} \text{ are invariant subgroups of the four group } V.
\end{align*}
\]

4.2.2.3. The Substitution Group \( G(M) \) of the Hamiltonian

The substitution group \( G(M) \) of the Hamiltonian is the proper product:

\[
G(M) = C^{(1)} P C^{(2)} P F
\]  

(4.28)

For the definition of products and proper products of subgroups of a group, see [13].
The proper product of $C^{(1)}$ and $C^{(2)}$ is equal to the product of $C^{(1)}$ and $C^{(2)}$, since their intersection contains only the unity $C^{(1)} \cap C^{(2)} = E$:

$$C^{(1)} \cap C^{(2)} = C^{(1)} \cdot C^{(2)}$$  \hspace{1cm} (4.29)

The proper product $(C^{(1)} \cdot C^{(2)}) \cap F$ is not always equal to the product $(C^{(1)} \cdot C^{(2)}) \cap F$; if $C^{(1)}$ and $C^{(2)}$ are both groups of even order ($n$ even in equation (4.22)) and $F = V$ or $F = C_{s3}$, it follows that

$$(C^{(1)} \cdot C^{(2)}) \cap F = C_{s3}$$  \hspace{1cm} (4.30)

The order of the group G(M) is:

$$\text{ord } G(M) = \frac{\text{ord } C^{(1)} \cdot \text{ord } C^{(2)} \cdot \text{ord } F}{\text{ord } ((C^{(1)} \cdot C^{(2)}) \cap F)}$$  \hspace{1cm} (4.31)

To avoid the proper product in the formula for G(M), we can replace F by $F'$; $F'$ is defined as the maximal subgroup of F for which the intersection with $(C^{(1)} \cdot C^{(2)})$ contains only the unit element; this definition is equivalent to the product relation:

$$F = F' \cdot ((C^{(1)} \cdot C^{(2)}) \cap F)$$  \hspace{1cm} (4.32)

Now, G(M) can be written as the product:

$$G(M) = C^{(1)} \cdot C^{(2)} \cdot F'$$  \hspace{1cm} (4.33)

The order of G(M) is:

$$\text{ord } G(M) = \text{ord } C^{(1)} \cdot \text{ord } C^{(2)} \cdot \text{ord } F'$$  \hspace{1cm} (4.34)

$C^{(1)}$ and $C^{(2)}$ are invariant subgroups of G(M); $F$ and $F'$ are subgroups of G(M); they are invariant subgroups of G(M) if and only if $\text{ord } C^{(1)} \leq 2$ and $\text{ord } C^{(2)} \leq 2$. 
The abstract group to which \( G(M) \) is isomorphous is independent of the choice of frame and internal rotor, although the elements of the group are not necessarily invariant under the exchange of frame and internal rotor (c.f. equations (4.23) and (4.24)). It should be pointed out that for some simple semi-rigid bodies it is possible to introduce a rotating co-ordinate system which is no more attached to one part of the body (frame) and to get a group \( G(M) \) of higher order than in the picture of frame and internal rotor.