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Study of the Restricted Non-Rigid Group of Tetramethyl Tungsten Hybrid

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A simple method is described for calculation of character tables for the symmetry group of molecules consisting of a number of CH_3 group attached to a rigid framework. The restricted non-rigid group of this molecule is seen to be a group of order 324 and it has a point-group symmetry C_{2v}. We prove that it is a group with 33 conjugacy classes and also computed the character tables of this group.

Key Words: Character table, Full non-rigid group, Tetramethyl tungsten hybrid.

INTRODUCTION

The non-rigid molecule group theory (NRG) in which the dynamical symmetry operations are defined as physical operations is a new field of chemistry. Some authors in a series of papers applied this theory to determine the character table of restricted NRG of some molecules[1-9].

A molecule undergoing such large amplitude movements, between various possible configurations, is known as a non-rigid molecule.

The complete set of molecular conversion operations, which commute with the nuclear motion operator, will contain overall rotation operations, describing the molecule rotating as a whole and intramolecular motion operations, describing molecular moieties moving with respect to the rest of the molecule. Such a set forms a group, which we call the full non-rigid group (f-NRG).

Group theory for non-rigid molecules is becoming more and more relevant and numerous applications to large amplitude vibrational in spectroscopy of small organic molecules are appearing in the literature[10-18]. As is well known, group theory for non-rigid molecules was essentially develop for two point of view: (i) The molecular symmetry group theory (MSG) of permutation inversion groups (PI) constructed by permutations and permutation-inversions of identical particles. The MSG group is then form by all feasible permutations and permutation-inversions[19,20].

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Longuet-Higgins[19] investigated the symmetry groups of non-rigid molecules, where changes from one conformation to another can occur easily. In many cases, these symmetry groups are not isomorphic with any of the familiar symmetry groups of rigid molecules and their character tables are not known. It is therefore of some interest and importance to develop simple methods of calculating these character tables, which are needed for classification of wave functions and determination of selection rules, (ii) The full and restricted non-rigid group theory (f-or r-NRG) built up with physical operations, expressed in terms of internal coordinates, that transform one conformation into another iso-energetic one.

The r-NRG is then formed by the complete set of physical operations which commute with given restricted or hamiltonian operators[2,3]. Lomont[21] has given two methods for calculating character tables. These are satisfactory for small groups, but both of them require knowledge of the class structure and hence of the group multiplication table and they become inaccessible as soon as the order of the group becomes even moderately large. For non-rigid molecules, whose symmetry groups may have several thousand elements, they are usually quite impracticable.

The alternative approach is less mechanical, requiring a certain amount of thought, but it is never the less simpler in practice. This involves two steps: first, the decomposition of the group into classes and second, the determination of sets of basis functions for certain representations, whose characters are then determined directly.

Stone[22] described a method, which is appropriate for molecules with a number of XH_3 groups attached to a rigid framework. It is not appropriate in cases where the framework is linear, as in ethane and dimethylacetylene.

In computing the character table of this molecule, the standard notation and terminology on character theory[23,24] is used.

The motivation for this study is outlined in[25-29] and the reader is encouraged to consult these papers for background material as well as basic computational techniques.

Theory

Throughout the present paper, the concepts of direct and semi-direct products will be used. For this purpose, let us consider two groups, I and G, which have no element in common except for the identity.

If I and G are such that any element Is commutes with any element Gr:

$$Is\ Gr = Gr\ Is$$

their product forms a group S which is the direct product of I and G:

$$I \times G = S$$

on the other hand, if I and G do not commute in detail but rather:

$$I\ Gr = Gr\ I$$

for all $Gr \in G$, then the group forms a set which is called the semi-direct

product of I and G, and is expressed as:

$$I \wedge G = S$$

where the invariant subgroup I with respect to G is written on left side.

Tetramethyl tungsten hybrid exhibits in its preferred conformation a structure with four equivalent methyl groups in *staggered* configuration (Fig. 1).

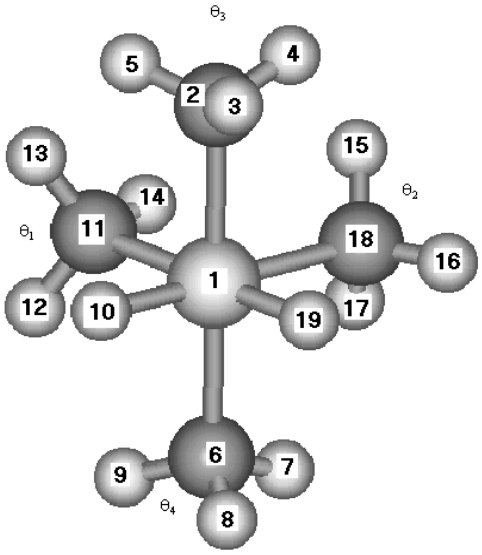

Fig. 1.

At first glance, the four rotations of the methyl group give us a large amplitude internal motion the variables which describe the four methyl rotations are the θ_1, θ_2, θ_3 and θ_4 angles, the four rotation axes being the W-CH_3 bonds.

The existence of the four equivalent methyl groups implies the existence of 81 iso-energetic.

Conformations, descried by four equivant C_3 non-rigid subgroup. When the methyl groups are distorted because of environmental effects, the C_3 symmetry has to be respected since the hydrogen atoms are indistinguishable[30].

$$\begin{aligned} C_{3_1}^{I} &= [\hat{E} + \hat{C}_{3_1} + \hat{C}_{3_1}^2], \\ C_{3_2}^{I} &= [\hat{E} + \hat{C}_{3_2} + \hat{C}_{3_2}^2], \\ C_{3_3}^{I} &= [\hat{E} + \hat{C}_{3_3} + \hat{C}_{3_3}^2], \\ C_{3_4}^{I} &= [\hat{E} + \hat{C}_{3_4} + \hat{C}_{3_4}^2] \end{aligned} \quad (1)$$

The direct product of these four subgroups contain 81 dynamical symmetry operations:

$$G_{81} = C_{3_1}^{I} \times C_{3_2}^{I} \times C_{3_3}^{I} \times C_{3_4}^{I} \quad (2)$$

which describe 81 potential energy wells on the potential energy hypersurface.

In order to establish the remaining transformation operations let us consider tetramethyl tungsten hybrid in an arbitrary conformation in which $\theta_1 \neq \theta_2 \neq \theta_3 \neq \theta_4$.

Since the four methyl groups are equivalent, the rotation angles may be interchanged by a 2-fold rotation without any energy variation:

$$\hat{W} f(\theta_1, \theta_2, \theta_3, \theta_4) = f(\theta_2, \theta_1, \theta_4, \theta_3) \quad (3)$$

θ_1 and θ_2 can not commute with θ_3 and θ_4 or by binary exchange (reflection) which induces an inversion of the rotation sense:

$$\hat{V} f(\theta_1, \theta_2, \theta_3, \theta_4) \equiv f(\theta_2, \theta_1, \theta_3, \theta_4) \quad (4)$$

being

$$W^I = [\hat{E} + \hat{W}] \quad (5)$$

$$V^I = [\hat{E} + \hat{V}]$$

The semi direct product of these two subgroups forms another subgroup isomorphic with the C_{2v} symmetry point group:

$$G_4 = [W^I \wedge V^I] \sim C_{2v} \quad (6)$$

which is the symmetry group of tetramethyl tungsten hybrid skeleton with unstructured methyl groups.

As a result, the complete r-NRG of tetramethyl tungsten hybrid may be written as

$$G_{324} = [W^I \wedge V^I] \wedge [C_{3_1}^{I} \times C_{3_2}^{I} \times C_{3_3}^{I} \times C_{3_4}^{I}] \quad (7)$$

which is a group of order 324.

Determination of conjugacy classes and character table of tetramethyl tungsten hybrid

First of all, we consider the point group of tetramethyl tungsten hybrid in the case of a rigid framework. We consider the restricted and full non-rigid group H (r-NRG and f-NRG) of this molecule each equilibrium conformation of which has an ordinary point-group symmetry C_{2v}.

Using Fig.1, we can write the following permutations:

a = (2,6)(3,8,4,9,5,7)(10,19)(11,18)(12,15,13,16,14,17)

b = (4,5)(7,9)(10,19)(11,18)(12,17,13,16,14,15)

Then by using the program of GAP[31], we can see that {a,b} is a generator set for the group H. That is H = <a,b>.

Since H is a permutation group, every two elements of this group with different cycle structure belong to different conjugacy classes. Hence, H is a group of order 324 and has exactly 33 conjugacy classes.

We show the cycle structure of the representatives of the conjugacy classes of H, in Table-1. In this table, cc stands for conjugacy classes, n is

their number and a permutation $\underbrace{(r_1,...,r_a)...(l_1,...,l_a)}_{b-number}\underbrace{(t_1,...t_c)...(s_1,...,s_c)}_{d-number}$ is denoted by $a^b.c^d$ for a,b,c,d ∈ N.

TABLE-1

cc	1	3	3^2	3^3	3^4	2^6	2^7	2^9	$2^3.6$	$2^4.6$	$2^6.6$
N	1	2	8	8	5	1	1	1	3	1	2

We have listed the representative of conjugacy classes of H in Table-2.

TABLE-2
REPRESENTATIVE OF CONJUGACY CLASSES OF THE GROUP H

No	Representative	Size
1	Identity	1
2	(15,16,17)	4
3	(12,13,14)(15,16,17)	2
4	(12,13,14)(15,17,16)	2
5	(7,8,9)	4
6	(7,8,9)(15,16,17)	4
7	(7,8,9)(15,17,16)	4
8	(7,8,9)(12,13,14)	4
9	(7,8,9)(12,13,14)(15,16,17)	4
10	(7,8,9)(12,13,14)(15,17,16)	4
11	(7,8,9)(12,14,13)	4
12	(7,8,9)(12,14,13)(15,16,17)	4
13	(7,8,9)(12,14,13)(15,17,16)	4
14	(4,5)(8,9)(10,19)(11,18)(12,15)(13,17)(14,16)	27
15	(4,5)(8,9)(10,19)(11,18)(12,15,13,17,14,16)	54
16	(3,4,5)(7,8,9)	2
17	(3,4,5)(7,8,9)(15,16,17)	4
18	(3,4,5)(7,8,9)(15,17,16)	4
19	(3,4,5)(7,8,9)(12,13,14)(15,16,17)	2
20	(3,4,5)(7,8,9)(12,13,14)(15,17,16)	4
21	(3,4,5)(7,8,9)(12,14,13)(15,17,16)	2
22	(3,4,5)(7,9,8)	2
23	(3,4,5)(7,9,8)(15,16,17)	4
24	(3,4,5)(7,9,8)(12,13,14)	4
25	(3,4,5)(7,9,8)(12,13,14)(15,16,17)	4
26	(3,4,5)(7,9,8)(12,13,14)(15,17,16)	4
27	(2,6)(3,7)(4,8)(5,9)(10,19)(11,18)(12,15)(13,16)(14,17)	9
28	(2,6)(3,7)(4,8)(5,9)(10,19)(11,18)(12,15,13,16,14,17)	18
29	(2,6)(3,7,4,8,5,9)(10,19)(11,18)(12,15)(13,16)(14,17)	18
30	(2,6)(3,7,4,8,5,9)(10,19)(11,18)(12,15,13,16,14,17)	18
31	(2,6)(3,7,4,8,5,9)(10,19)(11,18)(12,15,14,17,13,16)	18
32	(2,6)(3,7)(4,9)(5,8)(13,14)(16,17)	27
33	(2,6)(3,7,4,9,5,8)(13,14)(16,17)	54

The calculation of the character table of H by the following details in environment of GAP.

```
gap> H = Group (a,b);
gap> cc: = Conjugacy Classe (H);
gap> n: = List(cc, x->Size(x));
gap> tb: = Character Table(H);
gap> Display (tb);
```

The character table of G is listed in Table-3; (In Table-3, the conjugacy classes that contain elements of order n are named na,nb,nc,…).

TABLE-3
THE CHARACTER TABLE OF THE GROUP H
A = -E(3)+2*E(3)^2

	1a	3a	3b	3c	3d	3e	3f	3g	3h	3i	3j	3k	3l	2a	6a	3m	3n
X1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
X2	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
X3	1	1	1	1	1	1	1	1	1	1	1	1	1	-1	-1	1	1
X4	1	1	1	1	1	1	1	1	1	1	1	1	1	-1	-1	1	1
X5	2	-1	-1	2	-1	2	-1	2	-1	-1	-1	-1	2	·	·	-1	-1
X6	2	-1	-1	2	-1	2	-1	2	-1	-1	-1	-1	2	·	·	-1	-1
X7	2	2	2	2	-1	-1	-1	-1	-1	-1	-1	-1	-1	·	·	2	2
X8	2	2	2	2	-1	-1	-1	-1	-1	-1	-1	-1	-1	·	·	2	2
X9	2	-1	2	-1	2	-1	-1	-1	2	-1	-1	-1	2	-2	1	2	-1
X10	2	-1	2	-1	2	-1	-1	-1	2	-1	-1	-1	2	2	-1	2	-1
X11	2	2	2	2	-1	-1	-1	-1	-1	-1	-1	-1	-1	·	·	-1	-1
X12	2	2	2	2	-1	-1	-1	-1	-1	-1	-1	-1	-1	·	·	-1	-1
X13	2	-1	-1	2	-1	-1	2	-1	2	-1	2	-1	-1	·	·	-1	2
X14	2	-1	-1	2	-1	-1	2	-1	2	-1	2	-1	-1	·	·	-1	2
X15	2	-1	-1	2	2	-1	-1	-1	-1	2	-1	2	-1	·	·	2	-1
X16	2	-1	-1	2	2	-1	-1	-1	-1	2	-1	2	-1	·	·	2	-1
X17	4	-2	4	-2	-2	1	1	1	-2	1	1	1	-2	·	·	-2	1
X18	4	-2	-2	4	1	-2	1	-2	1	1	1	1	-2	·	·	-2	-2
X19	4	-2	4	-2	-2	1	1	1	-2	1	1	1	-2	·	·	4	-2
X20	4	1	-2	-2	-2	1	-2	1	4	1	-2	1	-2	·	·	-2	-2
X21	4	1	-2	-2	4	1	1	1	-2	-2	1	-2	-2	·	·	4	1
X22	4	4	4	4	1	1	1	1	1	1	1	1	1	·	·	-2	-2
X23	4	1	-2	-2	-2	-2	1	-2	-2	1	1	1	4	·	·	-2	1
X24	4	-2	-2	4	-2	1	1	1	1	-2	1	-2	1	·	·	4	-2
X25	4	-2	-2	4	1	1	-2	1	-2	1	-2	1	1	·	·	-2	4
X26	4	-2	4	-2	1	A	/A	/A	1	A	A	/A	1	·	·	-2	1
X27	4	-2	4	-2	1	/A	A	A	1	/A	/A	A	1	·	·	-2	1
X28	4	1	-2	-2	-2	A	A	/A	1	1	/A	1	1	·	·	4	1
X29	4	1	-2	-2	-2	/A	/A	A	1	1	A	1	1	·	·	4	1
X30	4	1	-2	-2	1	A	1	/A	-2	/A	1	A	1	·	·	-2	-2
X31	4	1	-2	-2	1	/A	1	A	-2	A	1	/A	1	·	·	-2	-2
X32	4	1	-2	-2	1	1	A	1	1	A	/A	/A	-2	·	·	-2	1
X33	4	1	-2	-2	1	1	/A	1	1	/A	A	A	-2	·	·	-2	1

	3o	3p	3q	3r	3s	3t	3u	3v	3w	2b	6b	6c	6d	6e	2c	6f
X1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
X2	1	1	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	-1	-1
X3	1	1	1	1	1	1	1	1	1	1	1	1	1	1	-1	-1
X4	1	1	1	1	1	1	1	1	1	-1	-1	-1	-1	-1	1	1
X5	2	2	-1	-1	2	-1	-1	-1	2	-2	1	1	-2	1	·	·
X6	2	2	-1	-1	2	-1	-1	-1	2	2	-1	-1	2	-1	·	·
X7	2	2	2	2	-1	-1	-1	-1	-1	·	·	·	·	·	-2	1
X8	2	2	2	2	-1	-1	-1	-1	-1	·	·	·	·	·	2	-1
X9	-1	2	-1	2	2	-1	-1	2	-1	·	·	·	·	·	·	·
X10	-1	2	-1	2	2	-1	-1	2	-1	·	·	·	·	·	·	·
X11	-1	-1	-1	-1	2	2	-1	2	-1	·	·	·	·	·	·	·
X12	-1	-1	-1	-1	2	2	2	2	2	-2	-2	1	1	1	·	·
X13	-1	-1	-1	2	2	-1	2	2	2	2	2	-1	-1	-1	·	·
X14	-1	-1	-1	2	2	-1	-1	-1	2	-2	1	1	1	-2	·	·
X15	-1	-1	2	-1	2	-1	-1	-1	2	2	-1	-1	-1	2	·	·
X16	-1	-1	2	-1	2	-1	-1	-1	2	-2	1	-2	1	1	·	·
X17	1	-2	1	-2	4	-2	-1	-1	2	2	-1	2	-1	-1	·	·
X18	4	4	-2	-2	-2	1	-2	4	-2	·	·	·	·	·	·	·
X19	-2	4	-2	4	-2	1	1	1	-2	·	·	·	·	·	·	·
X20	1	-2	1	4	4	1	1	-2	1	·	·	·	·	·	·	·
X21	1	-2	-2	-2	4	1	1	-2	-2	·	·	·	·	·	·	·
X22	-2	-2	-2	-2	-2	-2	-2	-2	-2	·	·	·	·	·	·	·
X23	-2	4	1	-2	4	1	1	-2	-2	·	·	·	·	·	·	·
X24	-2	-2	4	-2	-2	1	1	1	-2	·	·	·	·	·	·	·
X25	-2	-2	-2	4	-2	1	1	1	-2	·	·	·	·	·	·	·
X26	1	-2	1	-2	-2	1	1	-2	1	·	·	·	·	·	·	·
X27	1	-2	1	-2	-2	1	1	-2	1	·	·	·	·	·	·	·
X28	1	-2	-2	-2	-2	A	/A	1	1	·	·	·	·	·	·	·
X29	1	-2	-2	-2	-2	/A	A	1	1	·	·	·	·	·	·	·
X30	1	-2	1	4	-2	/A	A	1	1	·	·	·	·	·	·	·
X31	1	-2	1	4	-2	A	/A	1	1	·	·	·	·	·	·	·
X32	-2	4	1	-2	-2	/A	A	1	1	·	·	·	·	·	·	·
X33	-2	4	1	-2	-2	A	/A	1	1	·	·	·	·	·	·	·

Conclusions

The present character table for tetramethyl tungsten hybrid has been deduced from:

- the structure of the group

$$G_{324} = [W^{I} \wedge V^{I}] \wedge [\, C^{I}_{3_1} \times C^{I}_{3_2} \times C^{I}_{3_3} \times C^{I}_{3_4} \,]$$

- the division of the group in 33 classes, the sum of the squares of the dimensions of which gives the order of the group:

$$4\times(1)^2 + 12\times(2)^2 + 17\times(4)^2 = 324$$

- the composition of the 33 conjugacy classes in:

1, 4, 2, 2, 4, 4, 4, 4, 4, 4, 4, 4, 27, 54, 2, 4, 4, 2, 4, 2, 2, 4, 4, 4, 4, 9, 18, 18, 27 and 54 elements.

The potential energy function for rotation for XH_3 groups will be described by a 81-fold well potential energy hypersurface. As a result, the spectrum of the tetramethyl tungsten hybrid is expected to posses 32 substates.

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