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The Full Non-Rigid Group Theory for TBA (Tert-Butyl Alcohol)

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The non-rigid molecule group theory in which the dynamical symmetry operations are defined as physical operations is applied to deduce the character Table of the full non-rigid molecule group (f-NRG) of TBA. The f-NRG of this molecule is seen to be a group of order 54 which has 27 conjugacy classes.

Keywords: Character table, Conjugacy class, Full non-rigid group, TBA

INTRODUCTION

A non-rigid molecule is a molecular system which presents large amplitude vibration modes. This kind of motion appears whenever the molecule possesses various isoenergetic forms separated by relatively low-energy barriers. In such cases, intermolecular transformations occur.

Following Smeyers [1,2], the complete set of the molecular conversion operations that commute with the nuclear motion operator will contain overall rotation operations that describe the molecule rotating as a whole, and intermolecular motion operations that describe molecular moieties moving with respect to the rest of the molecule. Such a set forms a group, which we call the full non-rigid molecule group (f-NRG). Stone [3] has described a method which is appropriate for molecules with a number of XH3 groups attached to a rigid framework. An example of such molecules is TBA, which is considered in some detail. Although this method is not appropriate in cases where the framework is linear, as in ethane and dimethylacetylene, Bunker [4] has shown how to deal with such molecules. For computing the character Table of TBA molecule, we use some previously reported methods [5-6] for the standard notation and terminology on character theory.

In a series of papers [7-15], Balasubramanian has computed full non-rigid group of some molecules. For example, he computed the full non-rigid group for 1,3,5-triamino-2,4,6-trinitrobenzene [10], water pentamer [13] and extended aromatic $C_{48}N_{12}$ azafullerene [14]. Also Ashrafi and coauthors [16-25] computed full non-rigid group of some molecules. For example they computed the full non-rigid group of tetraammine platinum(II) [16], *cis*- and *trans*-dichloro-diammine platinum(II) and trimethylamine [17], tetraammine platinum(II) with C_{2v} and C_{4v} point group [19], tetraamine platinum(II) as wreath product [21], tetra-tert-butyltetrahedrane [22], tetramethylethylene [23], hexamethyl-benzene [24] and melamine [25].

In this paper the full non-rigid group of TBA is computed. Firstly the algebraic structure of the full non-rigid group of TBA is specified. Then, based on the structure of the group, a useful programming language, namely GAP [26], is applied and the character Table of f-NRG of this molecule is computed. The GAP package is used to find many properties of the groups.

The motivation for this study is outlined in previous publications [7-25] and the readers are encouraged to consult these papers for background material as well as basic computational techniques.

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METHODOLOGY

Firstly, we describe briefly some notation which will be used in the paper. A subgroup N of a group G is called normal if for any $g\in G$ and $x\in N$, $g^{-1}xg\in N$. Two elements x and y are said to be conjugate in G if there is an element g of G such that $y = g^{-1}xg$. For brevity, we write $x^g := g^{-1}xg$. It is easy to see that $(xy)^g = x^g y^g$, $(x^g)^h = x^{gh}$ and $(x^{-1})^g = (x^g)^{-1}$, for all $x,y,g,h\in G$. The conjugacy class of x is the set of all conjugates of x in G, denoted by $Cl_G(x)$. The element x is called a representative of $Cl_G(x)$. It is well known that $|Cl_G(x)| = |G|/|C_G(x)|$, where $C_G(x) = \{g\in G \mid xg = gx\}$ is the centralizer of x in G. The set of all conjugacy classes form a partition of G, so if $Cl_G(x_1), Cl_G(x_2), \ldots, Cl_G(x_r)$ are all distinct conjugacy classes of G , then $|G| = \sum_{i=1}^{r}|Cl_G(x_i)|$.

Suppose X is a set. The set of all permutations on X, denoted by S_X, is a group under the composition of functions, which is called the symmetric group on X. In the case that, $X = \{1, 2, \ldots, n\}$, we denote S_X by S_n or Sym(n). Every element π of S_n can be written uniquely as a product of disjoint cycles. If π is written as the product of $m_1, m_2, \ldots, m_s$ cycles of length $n_1, n_2, \ldots, n_s$, respectively, we say that π has cycle type $m_1^{n1} m_2^{n2} \ldots m_s^{ns}$. Two elements of S_n are conjugate in S_n if and only if they have the same cycle type.

Now consider the point group of the molecule in the case of a rigid framework. We consider the full non-rigid group G (f-NRG) of this molecule, each equilibrium conformation of which has an ordinary point group symmetry C_s. Since G is a permutation group, every two elements of this group with different cycle structure belong to different conjugacy classes of G. Referring to Fig. 1, the cycle structure of the representatives of the conjugacy classes of G is given. The permutations

$$x = (7,8,9),\ \ y = (10,11,12) \text{ and } z = (13,14,15)$$

rotate three methyl groups and the permutation and

$$w = (7,10)(9,11)(8,12)(13,15)(2,3)$$

(which is the reflection to plane containing the atoms 1, 4, 5, 6 and 14) are elements of G and generate the point group of

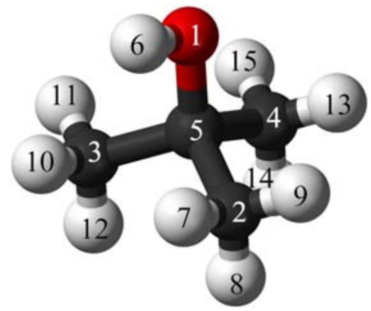

Fig. 1. The structure of TBA.

the molecule, that is G = <x, y, z, w>. At this time, we can use the GAP package and calculate the size and conjugacy classes of G. But in order to find conjugacy classes of G we may argue as follows. Since x, y, z are disjoint permutations, they commute with each other. Now since

$x^w = (10,12,11) = y^{-1}$, $y^w = (7,9,8) = x^{-1}$ and $z^w = (13,15,14) = z^{-1}$, we have

$Cl_G(x) = \{x,y^{-1}\}$, $Cl_G(y) = \{y,x^{-1}\}$ and $Cl_G(z) = \{z,z^{-1}\}$

Similarly using the identities

$(xy)^w = x^w y^w = x^{-1}y^{-1}$, $(x^{-1}y^{-1})^w = (x^{-1})^w(y^{-1})^w = xy$,
$(xz)^w = x^w z^w = y^{-1}z^{-1}$, $(y^{-1}z^{-1})^w = (y^{-1})^w(z^{-1})^w = xz$,
$(yz)^w = y^w z^w = x^{-1}z^{-1}$, $(x^{-1}z^{-1})^w = (x^{-1})^w(z^{-1})^w = yz$,
$(x^{-1}z)^w = (x^{-1})^w z^w = yz^{-1}$, $(yz^{-1})^w = y^w(z^{-1})^w = x^{-1}z$,
$(xz^{-1})^w = x^w(z^{-1})^w = y^{-1}z$, $(y^{-1}z)^w = (y^{-1})^w z^w = xz^{-1}$,
$(xyz)^w = x^w y^w z^w = x^{-1}y^{-1}z^{-1}$, $(x^{-1}y^{-1}z^{-1})^w = (x^{-1})^w(y^{-1})^w(z^{-1})^w = xyz$,
$(x^{-1}yz)^w = (x^{-1})^w y^w z^w = x^{-1}yz^{-1}$, $(x^{-1}yz^{-1})^w = (x^{-1})^w y^w(z^{-1})^w = x^{-1}yz$,
$(xy^{-1}z)^w = x^w(y^{-1})^w z^w = xy^{-1}z^{-1}$, $(xy^{-1}z^{-1})^w = x^w(y^{-1})^w(z^{-1})^w = xy^{-1}z$,
$(xyz^{-1})^w = x^w y^w(z^{-1})^w = x^{-1}y^{-1}z$, $(x^{-1}y^{-1}z)^w = (x^{-1})^w(y^{-1})^w z^w = xyz^{-1}$,
$(x^{-1}y)^w = (x^{-1})^w y^w = x^{-1}y$,
$(xy^{-1})^w = x^w(y^{-1})^w = xy^{-1}$,

we have

$Cl_G(xy) = \{xy,x^{-1}y^{-1}\}$, $Cl_G(xz) = \{xz,y^{-1}z^{-1}\}$, $Cl_G(yz) = \{yz,x^{-1}z^{-1}\}$, $Cl_G(x^{-1}z) = \{x^{-1}z, yz^{-1}\}$,

$Cl_G(xz^{-1}) = \{xz^{-1}, y^{-1}z\}$, $Cl_G(xyz) = \{xyz, x^{-1}y^{-1}z^{-1}\}$,
$Cl_G(x^{-1}yz) = \{x^{-1}yz, x^{-1}yz^{-1}\}$,
$Cl_G(xy^{-1}z) = \{xy^{-1}z, xy^{-1}z^{-1}\}$, $Cl_G(xyz^{-1}) = \{xyz^{-1}, x^{-1}y^{-1}z\}$,
$Cl_G(x^{-1}y) = \{x^{-1}y\}$, $Cl_G(xy^{-1}) = \{xy^{-1}\}$

It is easy to see that every conjugacy class of a non-identity element $x^cy^dz^e$, where $c,d,e \in \{-1,0,1\}$, is in the set of 15 conjugacy classes which we found asbove. Therefore G has 12 conjugacy classes of size 2 and 3 conjugacy clasess of size 1. From these conjugacy classes we see that G has 6 elements of cycle type 3^1, 12 elements of cycle type 3^2 and 8 elements of cycle type 3^3.

Similar arguments show that the elements w, xw and yw have distinct conjugacy classes of size 9. These conjugacy classes have 9 elements of cycle type 2^5 and 18 elements of cycle type 2^26^1. Simple calculations show that G has no conjugacy classes other than above conjugacy classes. So G has exactly 18 conjugacy classes. Since the set of conjugacy classes form a partition of G, we have $|G| = 3+12*2+3*9 = 54$.

We can summarize above results in Tables 1 and 2. The cycle types of non-identity elements of G are listed in Table 1. The representative and size of the conjugacy classes of G is given in Table 2. Note that we can do all of our computations by GAP [26].

RESULTS AND DISCUSSION

Let N be a normal subgroup of a group K. It is a well known fact that if η is a character of the factor group K/N, then the function χ defined by $\chi(k) = \eta(Nk)$ is a character of K, and χ and η have the same degree. In this case χ is an irreducible character of K if and only if η is an irreducible character of K/N (see [32, p. 24]). The Character χ of K is called the lifting of η to K. Thus using normal subgroups we can find some irreducible characters of K. This process is called lifting. Also it is well known that linear characters are obtained by lifting the irreducible characters of the factor group K modulus D, derived subgroup of K (see [5, p. 25]). Recall that the derived subgroup of K is the subgroup generated by all elements $u^{-1}v^{-1}uv$, where $u, v \in K$, that is $D = \langle u^{-1}v^{-1}uv | u, v \in K \rangle$.

In this section we find irreducible characters of G and relations between them. Since G has 18 conjugacy classes, it possesses 18 irreducible characters. We can find character Table of G using GAP. In Table 3, where the complete character Table of G is presented, the first row consists of representatives of each conjugacy class, but this time in the GAP notation a representative g is shown by the order of the element g. For example if an element g has order n, then its class is denoted by nx, where x runs over the letters a, b, *etc.* to denote the consecutive classes of elements of order n. If g belongs to the class nx and if m is 2, 3 or 5, then gm belongs to a class of elements of order n/(n,m), where (n,m) denotes the greatest common divisor of n and m, which are given in a column above nx. The values of the irreducible characters χi, $1 \le i \le 18$, at each class occupies the rest of Table 3. Note that In Table 3, /X denotes the complex conjugate of X. Also, the values A, B are as follows:

$A = (-1-i\sqrt{3})/2 = \varepsilon^2$, $B = -1+i\sqrt{3} = 2\varepsilon$, where $\varepsilon = e^{2\pi i/3}$ and $i = \sqrt{-1}$

Recall that for any element k of a group K we have $|C_K(k)| = |K|/|Cl_K(k)|$, where $C_K(k)$ is the centralizer of k in K and $Cl_K(k)$ is the conjugacy class containing k. If the number of conjugacy classes of K is t, then the conjugacy vector of K is a vector with t array such that every array is a conjugacy length for K. Similarly we can define centralizer vector of K. Now we find these vectors for full non-rigid group of the molecule. Suppose that V be conjugacy vector and U be centralizer vector of this group. Then we have

V = (1a, 3a, 3b, 3c, 3d, 3e, 3f, 3g, 3h, 3i, 3j, 3k, 3l, 3m, 3n, 2a, 6a, 6b)
U = (54, 27, 27, 27, 27, 27, 27, 27, 54, 27, 27, 27, 27, 54, 27, 6, 6, 6).

In order to find relations between irreducible characters of G we may argue as follows. Firstly we find linear characters of G. It is easy to see that the derived subgroup of G is $D = \langle xy,z \rangle = \langle (7,8,9)(10,11,12),(13,14,15) \rangle$. Since the size of factor group G modulus D is 6, G has exactly 6 irreducible characters of degree 1 (linear characters). Let us denote these characters by χ_1, χ_2, χ_3, χ_4, χ_5, and χ_6. Since the factor group G/D is a cyclic group of size 6, the set of all of linear irreducible characters of G is a cyclic group of size 6 and

Table 1. The Cycle Type of Non-Identity Elements of Full Non-Rigid Group of TBA

Cycle type	3^1	3^2	3^3	2^5	$2^2 6^1$
size	6	12	8	9	18

Table 2. Representative and Sizes of the Conjugacy Classes of Full Non-Rigid Group of TBA

No.	Representative	Size	No.	Representative	Size
1	()	1	10	(7,8,9)(10,12,11)(13,14,15)	2
2	(13,14,15)	2	11	(7,8,9)(10,11,12)	2
3	(10,12,11)	2	12	(7,8,9)(10,11,12)(13,14,15)	2
4	(10,12,11)(13,14,15)	2	13	(7,8,9)(10,11,12)(13,15,14)	2
5	(10,12,11)(13,15,14)	2	14	(7,9,8)(10,11,12)	1
6	(10,11,12)	2	15	(7,9,8)(10,11,12)(13,14,15)	2
7	(10,11,12)(13,14,15)	2	16	(7,10)(8,12)(9,11)(14,15)(2,3)	9
8	(10,11,12)(13,15,14)	2	17	(7,10,8,12,9,11)(14,15)(2,3)	9
9	(7,8,9)(10,12,11)	1	18	(7,10,9,11,8,12)(14,15)(2,3)	9

Table 3. Character Table of Full Non-Rigid Group of TBA

		1a	3a	3b	3c	3d	3e	3f	3g	3h	3i	3j	3k	3l	3m	3n	2a	6a	6b
	2P	1a	3a	3e	3g	3f	3b	3d	3c	3m	3n	3j	3k	3l	3h	3i	1a	3h	3m
	3P	1a	1a	1a	1a	1a	1a	1a	1a	1a	1a	1a	1a	1a	1a	1a	2a	2a	2a
	5P	1a	3a	3e	3g	3f	3b	3d	3c	3m	3n	3j	3k	3l	3h	3i	2a	6b	6a
χ_1		1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
χ_2		1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	-1	-1	-1
χ_3		1	1	A	A	A	/A	/A	/A	/A	/A	1	1	1	A	A	-1	-A	-/A
χ_4		1	1	/A	/A	/A	A	A	A	A	A	1	1	1	/A	/A	-1	-/A	-A
χ_5		1	1	A	A	A	/A	/A	/A	/A	/A	1	1	1	A	A	1	A	/A
χ_6		1	1	/A	/A	/A	A	A	A	A	A	1	1	1	/A	/A	1	/A	A
χ_7		2	-1	2	-1	-1	2	-1	-1	2	-1	2	-1	-1	2	-1	0	0	0
χ_8		2	-1	-1	2	-1	-1	-1	2	2	-1	-1	2	-1	2	-1	0	0	0
χ_9		2	-1	-1	-1	2	-1	2	-1	2	-1	-1	-1	2	2	-1	0	0	0
χ_{10}		2	2	-1	-1	-1	-1	-1	-1	2	2	-1	-1	-1	2	2	0	0	0
χ_{11}		2	-1	B	-/A	-/A	/B	-A	-A	/B	-A	2	-1	-1	B	-/A	0	0	0
χ_{12}		2	-1	/B	-A	-A	B	-/A	-/A	B	-/A	2	-1	-1	/B	-A	0	0	0
χ_{13}		2	-1	-/A	B	-/A	-A	-A	/B	/B	-A	-1	2	-1	B	-/A	0	0	0
χ_{14}		2	-1	-A	/B	-A	-/A	-/A	B	B	-/A	-1	2	-1	/B	-A	0	0	0
χ_{15}		2	-1	-/A	-/A	B	-A	/B	-A	/B	-A	-1	-1	2	B	-/A	0	0	0
χ_{16}		2	-1	-A	-A	/B	-/A	B	-/A	B	-/A	-1	-1	2	/B	-A	0	0	0
χ_{17}		2	2	-/A	-/A	-/A	-A	-A	-A	/B	/B	-1	-1	-1	B	B	0	0	0
χ_{18}		2	2	-A	-A	-A	-/A	-/A	-/A	B	B	-1	-1	-1	/B	/B	0	0	0

generated by χ_3. We have $\chi_2 = (\chi_3)^3$, $\chi_4 = (\chi_3)^5$, $\chi_5 = (\chi_3)^4$, $\chi_6 = (\chi_3)^2$. Now put

$A_1 = \langle (10,11,12), (7,8,9)(10,11,12) \rangle$

$A_2 = \langle (7,8,9)(10,12,11), (13,15,14) \rangle$

$A_3 = \langle (7,8,9)(10,12,11), (7,8,9)(10,11,12)(13,15,14) \rangle$

$A_4 = \langle (7,8,9)(10,12,11), (7,9,8)(10,12,11)(13,15,14) \rangle$.

The subgroups A_i, $i \in \{1,\ldots,4\}$, are normal subgroups of G, and the factor groups G modulus these subgroups are isomorphic to S_3, the symmetric group on three symbols.

Since S_3 has one irreducible character of degree 2, we obtain four irreducible characters of G by lifting the irreducible character of S_3 of degree 2 to G. We denote these irreducible characters by χ_7, χ_{10}, χ_8 and χ_9, respectively. If φ is a linear character of G, then the product $\varphi\chi_i$, i = 7, 8, 9, 10 are irreducible characters of G of degree 2. Using this fact, we can find all irreducible characters of G of degree 2. These characters are $\chi_{11} = \chi_7 \chi_4$, $\chi_{12} = \chi_7 \chi_3$, $\chi_{13} = \chi_8 \chi_4$, $\chi_{14} = \chi_8 \chi_3$, $\chi_{15} = \chi_9 \chi_4$, $\chi_{16} = \chi_9 \chi_3$, $\chi_{17} = \chi_{10} \chi_4$ and $\chi_{18} = \chi_{10} \chi_3$. Our calculations are summarized in Table 3.

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