

The Full Non-Rigid Group Theory for Tetraammine Platinum(II)

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The non-rigid molecule group theory (NRG), in which the dynamical symmetry operations are defined as physical operations, is a new field of chemistry. In a series of papers Smeyers applied this notion to determine the character table of restricted NRG of some molecules. In this work, a simple method is described, by means of which it is possible to calculate character tables for the symmetry group of molecules consisting of a number of NH_3 groups attached to a rigid framework. We have studied the full non-rigid group (f-NRG) of tetraammine platinum(II) with the symmetry group C_{2v} and we have proven that it is a group of order 216 with 27 conjugacy classes. We have also computed the character table of this group.

INTRODUCTION

A non-rigid molecule is a molecular system representing 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, intramolecular transformations occur.

The complete set of molecular conversion operations that commute with the nuclear motion operator will contain the 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 increasingly relevant, and numerous applications to large amplitude vibrational spectroscopy of small organic molecules are appearing in the literature.^{1–8}

In Ref. 9 Longuet-Higgins 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, determination of selection rules, and so on.

The method as described here is appropriate for molecules consisting of a number of XH_3 groups attached to a rigid framework. An example of such a molecule is tetraammine platinum(II), which is considered here in some detail. It is not appropriate in cases where the framework is linear, as it is in ethane, but Bunker¹⁰ has shown how to deal with such molecules. To compute the character table of this molecule, we use Refs. 11,12 for the standard notation and terminology of the character theory.

Lomont¹³ has proposed two methods for calculating character tables. These are satisfactory for a small group,

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but both of them require knowledge of the class structure and hence of the group multiplication table and they become very unwieldy as soon as the order of the group becomes even moderately large. They are usually quite impracticable for non-rigid molecules, whose symmetry groups may have several thousands of elements.

The alternative approach is less mechanical, requiring a certain amount of thought, but it is nevertheless 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.

In Ref. 14 Smeyers and Villa investigated the r-NRG of planar trimethylamine and proved that this is a group of order 324. Furthermore, they showed that this molecule has a pyramidal inversion and so the order of r-NRG of trimethylamine is 648. For basic properties of non-rigid molecule groups and information on r-NRG and f-NRG the reader is referred to Refs. 15,16.

In Ref. 17, Stone described a method 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 it is in ethane and dimethylacetylene.

The motivation for this study is outlined in Refs. 7, 8, 14–19 and the reader is encouraged to consult these papers for background material as well as basic computational techniques.

We now recall some algebraic definitions that will be used in the paper. Let G be a finite group and let N be a normal subgroup of G . If $|N| > 1$, then the factor group G/N is smaller than G . The characters of G/N should therefore be easier to find than the characters of G . In fact, we can use the characters of G/N to get some of the characters of G , by a process which is known as lifting. Thus, normal subgroups help us to find characters of G . To see this, we assume that χ is a character of G/N . Define $\phi: G \rightarrow \mathbb{C}$, \mathbb{C} is the field of complex numbers, by $\phi(g) = \chi(gN)$, for $g \in G$. Then χ is a character of G and χ and ϕ have the same degree. Character ϕ of G is called the lift of χ to G . It is a well-known fact that, χ is irreducible if and only if ϕ is irreducible (Ref. 12, p. 168).

In this paper, we investigate the f-NRG of tetraammine platinum(II). We prove that this is a group of order 216 and obtain its character table.

Throughout this paper, all groups considered are assumed to be finite. Our notation is standard and taken mainly from Refs. 11, 12 and 15.

EXPERIMENTAL

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

TABLE I. The cycle type of non-identity elements of H

2^4	2^6	2^8	3^2	3^3	3^4
$2^4 3^2$	$2^3 6^1$	$2^5 6^1$	$2^2 6^2$	$2^1 3^2 6^1$	$2^1 3^1 6^1$

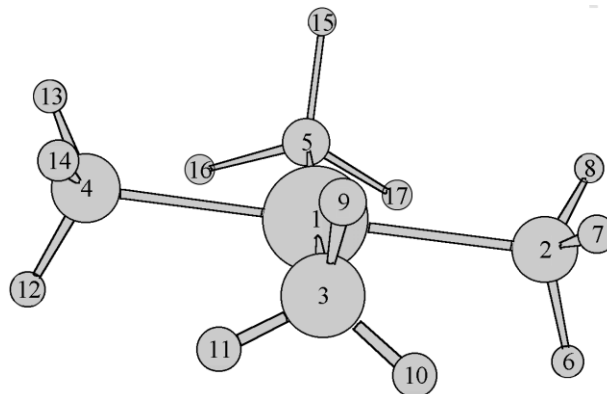


Figure 1. The structure of tetraammine platinum(II) with C_{2v} ordinary point group symmetry.

Since H is a permutation group, every two elements of this group with a different cycle structure belong to different conjugacy classes. Using Figure 1, we give the cycle structure of the representatives of the conjugacy classes of H in Table I.

Using Figure 1, we obtain a generating set for group H . Assume that

$$a_1 = (2,4)(3,5)(6,12)(9,15)(7,13)(10,16)(8,14)(11,17),$$

$$b_1 = (2,4)(3,5)(6,12,7,14,8,13)(9,15,10,17,11,16),$$

$$c_1 = (3,5)(7,8)(9,15)(10,17)(11,16)(13,14).$$

Then, with a simple Maple program, we can see that $\{a_1, b_1, c_1\}$ is a generating set for group H .

Now, using a computer calculation, we can see that H has exactly three conjugacy classes of elements of type 2^4 , two conjugacy classes of elements of type 2^6 , two conjugacy classes of elements of type 2^8 , and so on. In Table II, we give the representatives of every conjugacy class of H with their orders.

RESULTS AND DISCUSSION

For every element x of a group T , the subgroup $C_T(x) = \{y \in T \mid xy = yx\}$ is called the centralizer of x in T . If T is finite, then by a well-known theorem in group theory $|C_T(x)| = |T| / |Cl_T(x)|$, in which $Cl_T(x)$ is the conjugacy class of x in T .¹¹ Also, $|C_T(x)|$ and $|Cl_T(x)|$ are called the centralizer order and conjugacy length of x in group T , respectively. To simplify our argument, we denote by na, nb, nc, \dots the different conjugacy classes of elements of order n in group T . The conjugacy vector of T is a vector

TABLE II. Representatives of the conjugacy classes of group H

No.	Representatives	Size
1	()	1
2	(12,13,14)(15,16,17)	8
3	(9,10,11)(15,17,16)	2
4	(9,10,11)(12,14,13)(15,16,17)	4
5	(7,8)(10,11)(13,14)(16,17)	27
6	(6,7,8)(12,13,14)(15,17,16)	4
7	(6,7,8)(12,14,13)	2
8	(6,7,8)(9,10,11)(12,13,14)(15,16,17)	2
9	(6,7,8)(9,10,11)(12,14,13)(15,17,16)	4
10	(3,5)(9,15)(10,16)(11,17)	3
11	(3,5)(9,15,10,16,11,17)(12,13,14)	12
12	(3,5)(7,8)(9,15)(10,17)(11,16)(13,14)	9
13	(3,5)(7,8)(9,15,10,17,11,16)(12,13)	18
14	(3,5)(6,7,8)(9,15,11,17,10,16)(12,13,14)	6
15	(3,5)(6,7,8)(9,15)(10,16)(11,17)(12,14,13)	6
16	(2,4)(6,12)(7,13)(8,14)	3
17	(2,4)(6,12,7,13,8,14)(15,16,17)	12
18	(2,4)(6,12)(7,13)(8,14)(9,10,11)(15,17,16)	6
19	(2,4)(6,12,8,14,7,13)(9,10,11)(15,16,17)	6
20	(2,4)(6,12)(7,14)(8,13)(10,11)(16,17)	9
21	(2,4)(6,12,7,14,8,13)(10,11)(15,16)	18
22	(2,4)(3,5)(6,12)(7,13)(8,14)(9,15)(10,16)(11,17)	9
23	(2,4)(3,5)(6,12,7,13,8,14)(9,15,10,16,11,17)	18
24	(2,4)(3,5)(6,12)(7,14)(8,13)(9,15)(10,17)(11,16)	3
25	(2,4)(3,5)(6,12,7,14,8,13)(9,15,10,17,11,16)	12
26	(2,4)(3,5)(6,12)(7,14)(8,13)(9,16,10,15,11,17)	6
27	(2,4)(3,5)(6,12,8,13,7,14)(9,16)(10,15)(11,17)	6

of size k , k is the number of conjugacy classes of T, such that every array of this vector is a conjugacy length for T. Similarly, we can define the centralizer vector of T.

From the conjugacy classes of group H, we can see that H is a group of order 216. Suppose that \mathbf{A} denotes the conjugacy vector of H. Then

$$\mathbf{A} = (1a, 3a, 3b, 3c, 2a, 3d, 3e, 3f, 3g, 2b, 6a, 2c, 6b, 6c, 6d, 2d, 6e, 6f, 6g, 2e, 6h, 2f, 6i, 2g, 6j, 6k, 6l).$$

We now assume that \mathbf{B} is the centralizer vector of H. Using the first paragraph of this section, we can compute the components of this vector from the conjugacy lengths of this group. Thus, in Table II, we have:

$$\mathbf{B} = (216, 27, 108, 54, 8, 54, 108, 108, 54, 72, 18, 24, 12, 36, 36, 72, 18, 36, 36, 24, 12, 24, 12, 72, 18, 36, 36).$$

Since $H/H' \cong Z_2 \times Z_2 \times Z_2$, where Z_2 is a cyclic group of order 2, H has exactly eight linear characters, which we denote by $\chi_1, \chi_2, \dots, \chi_8$. It is a well-known fact that such χ_i 's are irreducible and one can compute these characters from the character table of group Z_2 . In what follows, we calculate the character table of H.

Suppose that $T_1 = \langle x_1, x_2, x_3 \rangle$, $T_2 = \langle y_1, y_2, y_3, y_4 \rangle$ and $T_3 = \langle x_1, y_1, y_3, z_1 \rangle$ are subgroups generated by $x_i, i = 1, 2, 3, y_i, i = 1, 2, 3, 4$ and $\{x_1, y_1, y_3, z_1\}$, in which x_i 's, y_i 's and z_1 are as follows:

$$x_1 = (3,5)(9,15)(10,16)(11,17),$$

$$x_2 = (2,4)(6,12)(7,14)(8,13)(10,11)(16,17),$$

$$x_3 = (6,7,8)(12,13,14)(15,17,16),$$

$$y_1 = (2,4)(6,12)(7,13)(8,14),$$

$$y_2 = (3,5)(7,8)(9,15)(10,17)(11,16)(13,14),$$

$$y_3 = (6,7,8)(12,14,13),$$

$$y_4 = (9,10,11)(12,14,13)(15,16,17),$$

$$z_1 = (9,11,10)(15,16,17).$$

It is an obvious fact that T_1, T_2 and T_3 are normal subgroups of H of order 36 and the factor groups H modulus $T_i, i = 1, 2, 3$, are isomorphic to S_3 , the symmetric group on three letters. On the other hand, if $A_i, i = 1, 2, 3$ are the set of all conjugacy classes of $T_i, i = 1, 2, 3$ then we can see that:

$$A_1 = \{1a, 3b, 3d, 3f, 2b, 6c, 2e, 2g, 6k\},$$

$$A_2 = \{1a, 3c, 3e, 3f, 2c, 2d, 6g, 2g, 6l\},$$

$$A_3 = \{1a, 3b, 3e, 3g, 2b, 6d, 2d, 6f, 2f\}.$$

Since S_3 has an irreducible character of degree 2, we can obtain three irreducible characters of H by lifting the irreducible character of S_3 of degree 2 to H. We denote these characters by χ_9, χ_{16} and χ_{20} . If ϕ is a linear character of H, then the Kronecker product $\phi\chi_i, i = 9, 16, 20$, is an irreducible character of H. Using this fact, we can obtain 12 irreducible characters of H of degree 2. These are $\chi_9, \chi_{10} = \chi_2\chi_9, \chi_{11} = \chi_8\chi_9, \chi_{12} = \chi_7\chi_9, \chi_{13} = \chi_5\chi_{16}, \chi_{14} = \chi_4\chi_{16}, \chi_{15} = \chi_2\chi_{16}, \chi_{16}, \chi_{17} = \chi_4\chi_{20}, \chi_{18} = \chi_3\chi_{20}, \chi_{19} = \chi_2\chi_{20}$ and χ_{20} . We now define $\chi_{21} = \chi_9\chi_{16}\chi_2, \chi_{22} = \chi_9\chi_{16}, \chi_{23} = \chi_3\chi_9\chi_{20}, \chi_{24} = \chi_9\chi_{20}, \chi_{25} = \chi_3\chi_{16}\chi_{20}$ and $\chi_{26} = \chi_{16}\chi_{20}$. By the definition of the Kronecker product, we can see that $\chi_{21}, \dots, \chi_{26}$ are irreducible characters of H of degree 4.

We now complete the character table of H. Since, H has exactly 27 conjugacy classes, it has 27 irreducible characters. Hence, it remains to compute one irreducible

TABLE III. The character table and power map of group H

	1a	3a	3b	3c	2a	3d	3e	3f	3g	2b	6a	2c	6b	6c	6d	2d	6e	6f	6g	2e	6h	2f	6i	2g	6j	6k	6l	
2p	1a	3a	3b	3c	1a	3d	3e	3f	3g	1a	3c	1a	3b	3f	3e	1a	3d	3b	3f	1a	3e	1a	3f	1a	3g	3b	3e	
3p	1a	1a	1a	1a	2a	1a	1a	1a	1a	2b	2b	2c	2c	2b	2b	2d	2d	2d	2d	2e	2e	2f	2f	2g	2g	2g	2g	
5p	1a	3a	3b	3c	2a	3d	3e	3f	3g	2b	6a	2c	6b	6c	6d	2d	6e	6f	6g	2e	6h	2f	6i	2g	6j	6k	6l	
χ_1	1	1	1	1	1	1	1	1	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	-1	-1	-1	-1	-1	-1	-1	-1	-1	
χ_3	1	1	1	1	-1	1	1	1	1	-1	-1	1	1	-1	-1	-1	-1	-1	1	1	1	1	-1	-1	-1	-1	-1	
χ_4	1	1	1	1	-1	1	1	1	1	-1	-1	1	1	-1	-1	1	1	1	1	-1	-1	-1	-1	1	1	1	1	
χ_5	1	1	1	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	-1	1	1	1	1	1	1	
χ_6	1	1	1	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	
χ_7	1	1	1	1	-1	1	1	1	1	1	1	-1	-1	1	1	1	1	1	1	-1	-1	1	1	-1	-1	-1	-1	
χ_8	1	1	1	1	-1	1	1	1	1	1	1	-1	-1	1	1	-1	-1	-1	-1	1	1	-1	-1	1	1	1	1	
χ_9	2	-1	-1	2	0	-1	2	2	-1	0	0	2	-1	0	0	2	-1	-1	2	0	0	0	0	2	-1	-1	2	
χ_{10}	2	-1	-1	2	0	-1	2	2	-1	0	0	2	-1	0	0	-2	1	1	-2	0	0	0	0	-2	1	1	-2	
χ_{11}	2	-1	-1	2	0	-1	2	2	-1	0	0	-2	1	0	0	-2	1	1	-2	0	0	0	0	2	-1	-1	2	
χ_{12}	2	-1	-1	2	0	-1	2	2	-1	0	0	-2	1	0	0	2	-1	-1	2	0	0	0	0	-2	1	1	-2	
χ_{13}	2	-1	2	-1	0	-1	2	-1	2	-2	1	0	0	1	-2	-2	1	-2	1	0	0	2	-1	0	0	0	0	
χ_{14}	2	-1	2	-1	0	-1	2	-1	2	-2	1	0	0	1	-2	2	-1	2	-1	0	0	-2	1	0	0	0	0	
χ_{15}	2	-1	2	-1	0	-1	2	-1	2	2	-1	0	0	-1	2	-2	1	-2	1	0	0	-2	1	0	0	0	0	
χ_{16}	2	-1	2	-1	0	-1	2	-1	2	2	-1	0	0	-1	2	2	-1	2	-1	0	0	2	-1	0	0	0	0	
χ_{17}	2	-1	2	-1	0	2	-1	2	-1	-2	1	0	0	-2	1	0	0	0	0	-2	1	0	0	2	-1	2	-1	
χ_{18}	2	-1	2	-1	0	2	-1	2	-1	-2	1	0	0	-2	1	0	0	0	0	2	-1	0	0	-2	1	-2	1	
χ_{19}	2	-1	2	-1	0	2	-1	2	-1	2	-1	0	0	2	-1	0	0	0	0	-2	1	0	0	-2	1	-2	1	
χ_{20}	2	-1	2	-1	0	2	-1	2	-1	2	-1	0	0	2	-1	0	0	0	0	2	-1	0	0	2	-1	2	-1	
χ_{21}	4	1	-2	-2	0	-2	-2	4	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	-4	-1	2	2
χ_{22}	4	1	-2	-2	0	-2	-2	4	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	4	1	-2	-2	
χ_{23}	4	1	-2	-2	0	1	4	-2	-2	0	0	0	0	0	0	-4	-1	2	2	0	0	0	0	0	0	0	0	
χ_{24}	4	1	-2	-2	0	1	4	-2	-2	0	0	0	0	0	0	4	1	-2	-2	0	0	0	0	0	0	0	0	
χ_{25}	4	1	4	1	0	-2	-2	-2	-2	-4	-1	0	0	2	2	0	0	0	0	0	0	0	0	0	0	0	0	
χ_{26}	4	1	4	1	0	-2	-2	-2	-2	4	1	0	0	-2	-2	0	0	0	0	0	0	0	0	0	0	0	0	
χ_{27}	8	-1	-4	2	0	2	-4	-4	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	

character. Since $|H| = 216 = \chi_1(1)^2 + \dots + \chi_{27}(1)^2$, χ_{27} is an irreducible character of degree 8. We claim that this character is rational valued. To see this, we note that if χ is an irreducible character of H, then the complex conjugate of χ is an irreducible character of the same degree. But H has a unique irreducible character of degree 8, so χ_{27} is rational valued. On the other hand, in the orthogonality relation (Ref. 12, p. 161), if g_1, \dots, g_{27} are representatives of the conjugacy classes of H, then for any $r, s \in \{1, 2, \dots, 27\}$, we have:

$$\chi_1(g_r) \chi_1(g_s) + \dots + \chi_{27}(g_r) \chi_{27}(g_s) = \delta_{rs} |C_H(g_r)|,$$

in which for all $r \in \{1, 2, \dots, 27\}$, $\delta_{rr} = 1$ and $\delta_{rs} = 0$. Using this relation, we can compute the irreducible char-

acter χ_{27} , which completes the character table of H. We summarize our calculations in Table III.

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SAŽETAK

Teorija potpune GNK za tetraamminoplatinat(II)

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Teorija grupa za gipke (non-rigid) molekule (GNK), gdje su operacije dinamičke simetrije definirane kao fizikalne operacije, predstavlja novo područje kemije. Ovo je područje započeo Smeyers koji je za niz gipkih molekula izračunao tablice karaktera pripadnih ograničenih GNK. Autori su opisali jednostavan postupak koji omogućava računanje tablica karaktera za grupe simetrije gipkih molekula u kojima je određen broj NH_3 skupina vezan na kruti skeleton. Posebice je proučena potpuna GNK za tetraamminoplatinat(II) grupe simetrije C_{2v} . Pokazano je da ova grupa sadrži 216 elemenata, koji se dijele u 27 klasa konjugiranih elemenata, i za nju je izračunana pripadna tablica karaktera.