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A study of the internal dynamics of trimethylamine by means of the non-rigid group theory

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The non-rigid molecule group theory (NRG) in which the dynamical symmetry operations are defined as physical operations is applied to determine the character table for the triple equivalent methyl rotation and pyramidal inversion in trimethylamine. The restricted NRG of this molecule is seen to be a group of order 648, formed as a product of two subgroups: the G_{324} subgroup corresponding to planar trimethylamine and the pyramidal inversion. For this purpose the structure of the r-NRG of planar trimethylamine is first deduced, i.e., the number of classes, irreducible representations, as well as their dimensions. Finally, guidelines are given to deduce systematically the symmetry eigenvectors developed on the basis of quadruple products of trigronometric functions. The r-NRG molecule group theory is seen to be used advantageously to study the internal dynamics of such small organic molecules.

KEY WORDS: large amplitude motions in trimethylamine, classes and character table for torsion–inversion in trimethylamine

1. Introduction

Group theory for non-rigid molecules is getting every day more and more relevance and numerous applications to large amplitude vibrations in spectroscopy of small organic molecules are appearing in the literature [1–4]. As is well known, group theory for non-rigid molecules was essentially developed from two points of view:

(i) The molecular symmetry group theory (MSG) of permutation–inversion group (PI) constructed by permutations and permutation–inversion of identical particles. The MSG group is then formed by all feasible permutations and permutations–inversions [5,6].

(ii) The full or 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 one isoenergetic. The r-NRG is then formed by the complete set of physical operations which commute with given restricted or Hamiltonian operator [7,8].

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Notice that the use of physical operations was initially suggested by Altmann [9]. But this author separated inopportunely the external and internal rotations and did not foresee that the r-NRG cannot be applied to non-rigid systems, which do not possess at least a two-dimensional frame [10]. Otherwise, the f-NRG has to be considered. Both theories are completely equivalent [7], although their application fields could be different.

Trimethylamine is a perfect example of non-rigid molecules to be studied by non-rigid group theory. Its group was never considered in detail in the literature. Only the group of planar trimethylborane, the closestly related molecule, was mentioned as an example in [5,9], and the neopentane molecule group was deduced into the permutations and permutation–inversion formalism [11].

The roto-torsional spectrum of trimethylamine was considered by microwave spectroscopy [12,13] and the torsional ones by infrared spectroscopy [14] using always symmetry point group. More recently rotational spectrum was again considered by microwave spectroscopy [15]. Lide et al. gave an analytical form for the potential energy function [12].

Nowadays spectroscopy measurements reach very high resolution. The purpose of this paper is to deduce the character table of trimethylamine, as well as its symmetry eigenvectors, using non-rigid group theory, similarly as done for methylamine [16] and acetone [17], in order to undertake its study from an updated point of view.

2. Theory

Trimethylamine exhibits in its preferred conformation a pyramidal structure with three equivalent methyl groups in “staggered” configuration, i.e., with two hydrogen atoms on each carbon atom pointing inwards (see figure 1) [12].

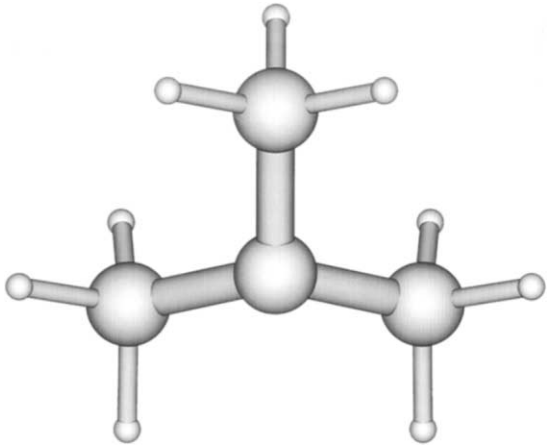

Figure 1. Trimethylamine in its staggered preferred conformation.

At first glance, trimethylamine presents two different types of large amplitude internal motions: the three rotations of the methyl groups and the symmetric inversion of the pyramidal structure. The variable which describes the inversion is the α angle defined by one of the N–CH_3 bonds and the planar structure. The variables which describe the three methyl rotations are the θ_1, θ_2 and θ_3 angles, the three rotation axes being the N–CH_3 bonds. The inversion angle origin is the planar structure and the origin for the rotation is the fully symmetric staggered preferred conformation (see figure 1).

The existence of the three equivalent methyl groups implies the existence of 27 isoenergetic conformations, described by three equivalent C_3 non-rigid subgroups. Notice that even when the methyl groups are distorded because of environmental effects, the C_3 symmetry has to be respected since the hydrogen atoms are indisguishible [18]:

$$\begin{aligned} C^I_{3_1} &= \left[\widehat{E} + \widehat{C}_{3_1} + \widehat{C}^{\,2}_{3_1}\right], \\ C^I_{3_2} &= \left[\widehat{E} + \widehat{C}_{3_2} + \widehat{C}^{\,2}_{3_2}\right], \\ C^I_{3_3} &= \left[\widehat{E} + \widehat{C}_{3_3} + \widehat{C}^{\,2}_{3_3}\right]. \end{aligned} \tag{1}$$

The direct product of these three subgroups contains 27 dynamical symmetry operations:

$$G_{27} = C^I_{3_1} \times C^I_{3_2} \times C^I_{3_3}, \tag{2}$$

which describe 27 potential energy wells on the potential energy hypersurface.

In order to establish the remaining transformation operations let us consider trimethylamine in an arbitrary conformation in which $\theta_1 \neq \theta_2 \neq \theta_3$. Since the three methyl groups are equivalent the rotation angles may be interchanged by a threefold rotation without any energy variation:

$$\begin{aligned} \widehat{W} f(\theta_1, \theta_2, \theta_3) &\equiv f(\theta_3, \theta_1, \theta_2), \\ \widehat{W}^2 f(\theta_1, \theta_2, \theta_3) &\equiv f(\theta_2, \theta_3, \theta_1) \end{aligned} \tag{3}$$

or by binary exchange (reflection) which induces an inversion of the rotation sense:

$$\widehat{U} f(\theta_1, \theta_2, \theta_3) \equiv f(\theta_1, \theta_3, \theta_2), \tag{4}$$

being

$$\begin{aligned} W^I &= \left[\widehat{E} + \widehat{W} + \widehat{W}^{\,2}\right], \\ U^I &= \left[\widehat{E} + \widehat{U}\,\right]. \end{aligned} \tag{5}$$

The semidirect product of these two subgroups forms another subgroup isomorphic with the C_{3v} symmetry point group:

$$G_6 = \left[W^I \wedge U^I\right] \sim C_{3v}, \tag{6}$$

which is the symmetry group of trimethylamine skeleton with unstructured methyl groups, regardless the pyramidal inversion.

Furthermore, since there exist symmetry planes in the rotor and the frame, the triple inversion of the methyl rotation angles does not imply any change in energy, so that the triple inversion defines the NRG subgroup [19]:

$$\widehat{V} f(\theta_1, \theta_2, \theta_3) \equiv f(-\theta_1, -\theta_2, -\theta_3). \tag{7}$$

Finally, the inversion of the pyramidal structure with a simultaneous C_2 rotations of the three methyl groups does not imply any change in energy too, as a result, this operation defines another NRG operation:

$$\widehat{I} f(\theta_1, \theta_2, \theta_3, \alpha) \equiv f(\theta_1 + \pi, \theta_3 + \pi, \theta_2 + \pi, -\alpha), \tag{8}$$

being

$$I^I = \left[\widehat{E} + \widehat{I}\right]. \tag{9}$$

As a result, the complete r-NRG of trimethylamine may be written as

$$G_{648} = \left[U^I \wedge W^I\right] \wedge I^I \wedge \left[C^I_{3_1} \times C^I_{3_2} \times C^I_{3_3}\right] \times V^I \tag{10}$$

which is a group of order 648.

3. The planar trimethylamine r-NRG character table

In order to deduce the character table of planar trimethylamine (or trimethylborane) we have to know first the number of classes, as well as the number of elements in each class. As well known, the number of classes will give the number of irreducible representations. Finally, we have to deduce the dimension of each irreducible representation.

3.1. Deduction of the classes

To deduce the classes, the NRG operations were divided conveniently into 4 sets:

$$\begin{aligned} A &\to W^I \wedge G_{27}, \\ B &\to \left[W^I \wedge G_{27}\right]\widehat{V}, \\ C &\to \widehat{U}\left[W^I \wedge G_{27}\right], \\ D &\to \widehat{U}\left[W^I \wedge G_{27}\right]\widehat{V}, \end{aligned} \tag{11}$$

where G_{27} and W^I are the subgroups (2) and (5), but $\widehat{U}$ and $\widehat{V}$ are the operations (4) and (8). The character $\wedge$ means semidirect product.

The multiplication of the first set by all similarity operations of the group permits to separate its elements into eigth classes:

$$
\begin{aligned}
a_0 &= \widehat{E},\\
a_1 &= \left[\widehat{C}_1 + \widehat{C}_1^{\,2}\right] + \left[\widehat{C}_2 + \widehat{C}_2^{\,2}\right] + \left[\widehat{C}_3 + \widehat{C}_3^{\,2}\right]\\
&\equiv a_{11} + a_{12} + a_{13},\\
a_2 &= \left[\widehat{C}_1\widehat{C}_2 + \widehat{C}_1^{\,2}\widehat{C}_2^{\,2}\right] + \left[\widehat{C}_1\widehat{C}_3 + \widehat{C}_1^{\,2}\widehat{C}_3^{\,2}\right] + \left[\widehat{C}_2\widehat{C}_3 + \widehat{C}_2^{\,2}\widehat{C}_3^{\,2}\right]\\
&\equiv a_{21} + a_{22} + a_{23},\\
a_3 &= \left[\widehat{C}_1\widehat{C}_2{}^2 + \widehat{C}_1^{\,2}\widehat{C}_2\right] + \left[\widehat{C}_1\widehat{C}_3{}^2 + \widehat{C}_1^{\,2}\widehat{C}_3\right] + \left[\widehat{C}_2\widehat{C}_3{}^2 + \widehat{C}_2^{\,2}\widehat{C}_3\right]\\
&\equiv a_{31} + a_{32} + a_{33},\\
a_4 &= \left[\widehat{C}_1\widehat{C}_2\widehat{C}_3 + \widehat{C}_1{}^2\widehat{C}_2{}^2\widehat{C}_3{}^2\right]\\
&\equiv a_{41},\\
a_5 &= \left[\widehat{C}_1\widehat{C}_2\widehat{C}_3{}^2 + \widehat{C}_1{}^2\widehat{C}_2{}^2\widehat{C}_3\right] + \left[\widehat{C}_1\widehat{C}_2{}^2\widehat{C}_3 + \widehat{C}_1{}^2\widehat{C}_2\widehat{C}_3{}^2\right]\\
&\quad + \left[\widehat{C}_1{}^2\widehat{C}_2\widehat{C}_3 + \widehat{C}_1\widehat{C}_2{}^2\widehat{C}_3{}^2\right]\\
&\equiv a_{51} + a_{52} + a_{53},\\
a_6 &= \left[\widehat{W} + \widehat{W}^2\right][a_0 + a_3 + a_4],\\
a_7 &= \left[\widehat{W} + \widehat{W}^2\right][a_1 + a_2 + a_5],
\end{aligned}
\tag{12}
$$

where each operation with its inverse is symbolized by one letter with two indices.

In the same way, the multiplication of the second set by all the similarity operations of the group permits us to select two classes:

$$
b_1 = [G_{27}]\ \widehat{V}, \qquad b_2 = \left[\widehat{W} + \widehat{W}^2\right][G_{27}]\widehat{V}. \tag{13}
$$

Identically, the multiplication of the third set yields five classes:

$$
\begin{aligned}
c_1 &= \widehat{U}[a_0 + a_{33}] + \widehat{U}\widehat{W}\ [a_0 + a_{32}] + \widehat{U}\widehat{W}^2\ [a_0 + a_{31}],\\
c_2 &= \widehat{U}[a_{11} + a_{52} + a_{51}] + \widehat{U}\widehat{W}[a_{12} + a_{51} + a_{53}] + \widehat{U}\widehat{W}^2[a_{13} + a_{52} + a_{53}],\\
c_3 &= \widehat{U}[a_{12} + a_{13} + a_{23}] + \widehat{U}\widehat{W}[a_{11} + a_{13} + a_{21}] + \widehat{U}\widehat{W}^2[a_{11} + a_{12} + a_{22}],\\
c_4 &= \widehat{U}[a_{21} + a_{22} + a_{53}] + \widehat{U}\widehat{W}[a_{21} + a_{23} + a_{52}] + \widehat{U}\widehat{W}^2[a_{22} + a_{23} + a_{51}],\\
c_5 &= \widehat{U}[a_{31} + a_{32} + a_{41}] + \widehat{U}\widehat{W}[a_{31} + a_{33} + a_{41}] + \widehat{U}\widehat{W}^2[a_{32} + a_{33} + a_{41}],
\end{aligned}
\tag{14}
$$

Finally, the multiplication of the fourth set furnishes two classes:

$$
\begin{aligned}
d_1 = {} & \widehat{U}\ [a_0 + a_{11} + a_{23} + a_{41} + a_{53}]\widehat{V}\\
& + \widehat{U}\widehat{W}[a_0 + a_{12} + a_{22} + a_{41} + a_{52}]\widehat{V}\\
& + \widehat{U}\widehat{W}^2[a_0 + a_{13} + a_{21} + a_{41} + a_{51}]\widehat{V}
\end{aligned}
\tag{15}
$$

and

$$
\begin{aligned}
d_2 = {} & \widehat{U}[a_{12} + a_{21} + a_{31} + a_{13} + a_{22} + a_{32} + a_{33} + a_{52} + a_{51}]\widehat{V}\\
& + \widehat{U}\widehat{W}[a_{11} + a_{21} + a_{31} + a_{13} + a_{32} + a_{23} + a_{33} + a_{51} + a_{53}]\widehat{V}\\
& + \widehat{U}\widehat{W}^2[a_{11} + a_{12} + a_{31} + a_{22} + a_{32} + a_{52} + a_{53} + a_{33} + a_{23}]\widehat{V}.
\end{aligned}
\tag{16}
$$

Seventeen classes are then obtained.

3.2. Rules for deducing the symmetry eigenvectors

As well known the sum of the squares of the dimensions of all the classes has to be equal to the order of the group: 324. One way to satisfy this requirement is the following set:

$$4 \times (1)^2 + 4 \times (2)^2 + 1 \times (4)^2 + 8 \times (6)^2 = 324.$$

In order to separate the possible irreducible representations, it is convenient to distinguish four types of possible symmetry eigenvectors:

(1) The functions conserve the C_3 symmetry of the three methyl groups.

(2) The functions conserve the C_3 symmetry of only two of them.

(3) The functions conserve the C_3 symmetry of only one of them.

(4) The functions do not exhibit any C_3 symmetry at all.

In the following K, L and M will be always integers multiple of three, i.e., $K = \dot{3}$, $L = \dot{3}$ and $M = \dot{3}$.

3.2.1. The function conserves the C_3 symmetry of the three methyl groups

In this case, the symmetry eigenvectors may be classified according to irreducible representations of the G_{12} r-NRG of the trimethylamine skeleton:

$$G_{12} = \left(U^I \wedge W^I\right) \times V^I \sim D_{3h}. \tag{17}$$

If the functions are developed onto the basis of the triple free rotor solutions, i.e., products of the three trigonometric functions, the following expressions can be written for the A_1 and A_2 representations:

$$\begin{aligned}\chi_{(A_1),(A_2)} = {} & [\cos K\theta_1 \cos L\theta_2 \cos M\theta_3 + \cos L\theta_1 \cos M\theta_2 \cos K\theta_3 \\ & + \cos M\theta_1 \cos K\theta_2 \cos L\theta_3] \pm [\cos M\theta_1 \cos L\theta_2 \cos K\theta_3 \\ & + \cos L\theta_1 \cos K\theta_2 \cos M\theta_3 + \cos K\theta_1 \cos M\theta_2 \cos L\theta_3],\end{aligned} \tag{18}$$

where the positive and negative signs correspond to A_1 and A_2 representations, respectively.

For the E_1 representation we have two components:

$$\chi_{(E_1)} = \begin{cases} \big[\cos K\theta_1 \cos L\theta_2 \cos M\theta_3 \\ \quad -\frac{1}{2}(\cos L\theta_1 \cos M\theta_2 \cos K\theta_3 + \cos M\theta_1 \cos K\theta_2 \cos L\theta_3)\big], \\ [\cos L\theta_1 \cos M\theta_2 \cos K\theta_3 - \cos M\theta_1 \cos K\theta_2 \cos L\theta_3]. \end{cases} \tag{19}$$

For more generality, three equivalent sets for the A_1 or A_2 and E_1 representations including all the cos × sin × sin symmetric products have to be added to these three symmetry eigenvectors.

In the same way, the A_3, A_4 and E_2 can be written as antisymmetric products of sin × cos × cos or sin × sin × sin functions.

3.2.2. The functions conserve the C_3 symmetry of only two methyl groups

In this case, the properties of the A and G irreducible representations for the double rotation in acetone can be used advantageously [7,17]. From the A_1 representation, in which the two methyl groups conserve the C_3 symmetry, three eigenvector components for the triple rotation may be written by simple application of the W^I subgroup operations:

$$\chi_I = \begin{cases} \big[(\cos K\theta_1 \cos L\theta_2 + \cos L\theta_1 \cos K\theta_2)\cos(M+1)\theta_3\big], \\ \big[(\cos K\theta_2 \cos L\theta_3 + \cos L\theta_2 \cos K\theta_3)\cos(M+1)\theta_1\big], \\ \big[(\cos K\theta_3 \cos L\theta_1 + \cos L\theta_3 \cos K\theta_1)\cos(M+1)\theta_2\big]. \end{cases} \tag{20}$$

They are symmetric with respect to the $\widehat{V}$ operation.

Taking into account the properties of the G representations, three antisymmetric vectors with respect to $\widehat{V}$ may be associated to the former, replacing $\cos(M+1)\theta$ by $\sin(M+1)\theta$. It is easily verified that these six vectors are energetically degenerate. They form a set for the components of the sixfold degenerate I_1 representation.

The $\widehat{W}$ operator transforms the components into themselves. They are symmetric or antisymmetric with respect to the $\widehat{V}$ operation and two of them are symmetric with respect to the $\widehat{U}$ operation.

For more generality, notice that another set of vectors, with the same symmetry properties can be written from the A_2 and G representations of acetone.

In the same way, from the A_3 or A_4 and G representations of acetone, two sets of sixfold energetically degenerate components can be written, with the same symmetry properties except that two of them are now antisymmetric with respect to the $\widehat{U}$ operation. They form a set for the sixfold degenerate I_2 representation.

3.2.3. The functions conserve the C_3 symmetry of only one methyl group

In this case, the properties of the E and G irreducible representations for the double rotations in acetone can be also used [7,17].

From the E_1 representation, in which only one methyl group conserves the C_3 symmetry the two following components for the triple rotation may be written:

$$\chi_{I'} = \begin{cases} \big[\cos(K+1)\theta_1 \cos(L+1)\theta_2 + \cos(L+1)\theta_1 \cos(K+1)\theta_2 \\ \quad + \sin(K+1)\theta_1 \sin(L+1)\theta_2 + \sin(L+1)\theta_1 \sin(K+1)\theta_2\big]\cos M\theta_3, \\ \big[\cos(K+1)\theta_1 \sin(L+1)\theta_2 + \sin(L+1)\theta_1 \cos(K+1)\theta_2 \\ \quad - \sin(K+1)\theta_1 \cos(L+1)\theta_2 - \sin(L+1)\theta_1 \cos(K+1)\theta_2\big]\cos M\theta_3. \end{cases} \tag{21}$$

These two components are symmetric and antisymmetric with respect to the $\widehat{V}$ operation, respectively. To these two components, four others can be added by applying the $\widehat{W}$ and $\widehat{W}^2$ operations. Two of them are symmetric and antisymmetric with respect to the $\widehat{U}$ operation, but they are symmetric with respect to $\widehat{U}\widehat{V}$ operation.

From the acetone G representation properties they can be easily verified to be energetically degenerate. They form a set for the sixfold I_1' representation.

From the E_2 representation of acetone six symmetry eigenvectors can be deduced, in the same way, for the triple methyl rotation. They are symmetric and antisymmetric with respect to the $\widehat{V}$ operation. The $\widehat{W}$ operations transfrom one of them into another. Two of them are symmetric and antisymmetric with respect to the $\widehat{U}$ operation, but antisymmetric with respect the $\widehat{V}\widehat{U}$ operation. They are energetically degenerate and form a set for the sixfold I_2' representation.

From the E_3 represention of acetone, six symmetry eigenvectors can be deduced. They are symmetric and antisymmetric with respect to the $\widehat{V}$ operator, the $\widehat{W}$ operators transfrom them into themselves, and two of them are symmetric with respect to the $\widehat{U}$ operation. They are energetically degenerate and form a set for the sixfold I_3' representation.

From the E_4 repesentation of acetone, six symmetry eigenvectors can be deduced, with the same symmetry properties except that two of them are now antisymmetric with respect to the $\widehat{U}$ operation. They form a set for the I_4' repesentation.

3.2.4. The functions do not exhibit any C_3 symmetry at all for the methyl groups

Two subcases have to be distinguished. The three methyl groups exhibit a threefold symmetry increased in one unit or two units.

In the first subcase, the A and E irreducible representations of planar trimethylamine will be used to construct the symmetry eigenvectors.

From the A_1 and A_3 representations of trimethylamine two vectors can be built with even or odd products of trigonometric functions. For example, for the even products we have:

$$\chi_{(E_1)} = \begin{cases} \big[\cos(K+1)\theta_1 \cos(L+1)\theta_2 \cos(M+1)\theta_3 \\ \quad + \cos(L+1)\theta_1 \cos(M+1)\theta_2 \cos(K+1)\theta_3 \\ \quad + \cos(M+1)\theta_1 \cos(K+1)\theta_2 \cos(L+1)\theta_3 \\ \quad + \cos(M+1)\theta_1 \cos(L+1)\theta_2 \cos(K+1)\theta_3 \\ \quad + \cos(L+1)\theta_1 \cos(K+1)\theta_2 \cos(M+1)\theta_3 \\ \quad + \cos(K+1)\theta_1 \cos(M+1)\theta_2 \cos(L+1)\theta_3\big], \\ \text{and odd products}. \end{cases} \tag{22}$$

Both vectors are energetically degenerate. They are symmetric with respect the $\widehat{W}$ and $\widehat{U}$ operators, but symmetric and antisymmetric with respect to $\widehat{V}$. They form a set for the E_1'' representation.

In the same way, from the A_2 and A_4 representations of trimethylamine, two vectors can be built symmetric with respect to $\widehat{W}$, but antisymmetric with respect to the $\widehat{U}$ operation. They form a set for the E_2'' repesentation.

Finally, from the E_1 and E_2 representations of trimethylamine four isoenergetic vectors can be constructed. They form a set for the tetra-degenerate G representation.

In second subcase, the I_1 and I_2 representations of trimethylamine have to be considered. From the I_1 representation, six energetically degenerate vectors can be built:

$$\chi_{I''} = \begin{cases} \left[\cos(K+1)\theta_1 \cos(L+1)\theta_2 + \cos(L+1)\theta_1 \cos(K+1)\theta_2\right] \cos(M+2)\theta_3, \\ \left[\sin(K+1)\theta_1 \sin(L+1)\theta_2 + \sin(L+1)\theta_1 \sin(K+1)\theta_2\right] \cos(M+2)\theta_3, \\ \left[\cos(K+1)\theta_1 \cos(L+1)\theta_3 + \cos(L+1)\theta_1 \cos(K+1)\theta_3\right] \cos(M+2)\theta_2, \\ \left[\sin(K+1)\theta_1 \sin(L+1)\theta_3 + \sin(L+1)\theta_1 \sin(K+1)\theta_3\right] \cos(M+2)\theta_2, \\ \left[\cos(K+1)\theta_2 \cos(L+1)\theta_3 + \cos(L+1)\theta_2 \cos(K+1)\theta_3\right] \cos(M+2)\theta_1, \\ \left[\sin(K+1)\theta_2 \sin(L+1)\theta_3 + \sin(L+1)\theta_2 \sin(K+1)\theta_3\right] \cos(M+2)\theta_1, \\ \text{and odd products.} \end{cases} \tag{23}$$

The remaining three vectors antisymmetric with respect to $\widehat{V}$ may be easily obtained by replacing $\cos(M+2)\theta$ by $\sin(M+2)\theta$. They have the same symmetry properties that the respresentation I_1 with respect to the $\widehat{W}$, $\widehat{U}$ and $\widehat{V}$ operations. In particular, two of them are symmetric with respect to the $\widehat{U}$ operation. They form a set for the I_1'' representation.

In the same way, from the I_2 representation of trimethylamine, six symmetry eigenvectors may be deduced. They have the same symmetry properties that the I_1'' representation except that two of them are antisymmetric with respect to the $\widehat{U}$ operation. They form a set for the I_2'' representation.

3.3. *The character table for trimethylamine*

From the symmetry eigenvectors the characters of each representation are easily deduced for all the classes by simple application of the symmetry operations. In addition, the orthogonality rules between the different representations may be used. The resulting character table is given in table 1.

To verify these results the linear equation system defined by the characters of each representation is solved to obtain the dimensions of the classes.

In a tentative calculation, by using a small basis set (6-31G**) at the RHF level, the staggered conformation was verified to be the most stable one, and the coefficients of the full potential energy function for the triple methyl rotation (18) were determined:

$$\begin{aligned} V(\theta_1, \theta_2, \theta_3) = \sum A_{K,L,M} [&\cos K\theta_1 \cos L\theta_2 \cos M\theta_3 + \cos L\theta_1 \cos M\theta_2 \cos K\theta_3 \\ &+ \cos M\theta_1 \cos K\theta_2 \cos L\theta_3 + \cos M\theta_1 \cos L\theta_2 \cos K\theta_3 \\ &+ \cos L\theta_1 \cos K\theta_2 \cos M\theta_3 + \cos K\theta_1 \cos M\theta_2 \cos L\theta_3 \\ &+ \sin K\theta_1 \sin L\theta_2 \cos M\theta_3 + \sin L\theta_1 \cos M\theta_2 \sin K\theta_3 \\ &+ \cos M\theta_1 \sin K\theta_2 \sin L\theta_3 + \cos M\theta_1 \sin L\theta_2 \sin K\theta_3 \\ &+ \sin L\theta_1 \sin K\theta_2 \cos M\theta_3 + \sin K\theta_1 \cos M\theta_2 \sin L\theta_3 \\ &+ \cos K\theta_1 \sin L\theta_2 \sin M\theta_3 + \sin L\theta_1 \sin M\theta_2 \cos K\theta_3 \\ &+ \sin M\theta_1 \cos K\theta_2 \sin L\theta_3 + \sin M\theta_1 \sin L\theta_2 \cos K\theta_3 \end{aligned}$$

$$+ \sin L\theta_1 \cos K\theta_2 \sin M\theta_3 + \cos K\theta_1 \sin M\theta_2 \sin L\theta_3$$
$$+ \sin K\theta_1 \cos L\theta_2 \sin M\theta_3 + \cos L\theta_1 \sin M\theta_2 \sin K\theta_3$$
$$+ \sin M\theta_1 \sin K\theta_2 \cos L\theta_3 + \sin M\theta_1 \cos L\theta_2 \sin K\theta_3$$
$$+ \cos L\theta_1 \sin K\theta_2 \sin M\theta_3 + \sin K\theta_1 \sin M\theta_2 \cos L\theta_3 \quad (24)$$

This expression may be regarded as an extension of that given in [12]. A reasonable value for the torsional barrier height is found (4.2 kcal/mol), when compared with data from experiments (4.4 kcal/mol) [12,14].

Solving the corresponding Hamiltonian equation, the four lowest energy levels were obtained. These levels presented a six-fold near degenerate substructure. For the fundamental, six sublevels of A_1, I_1, I_1', I_2', I_1'' and E_1'' symmetries were found in accordance with the character table.

4. The r-NRG for pyramidal trimethylamine

In the previous calculations, the inversion barrier was found to be lower than the barrier for the triple methyl rotation. This feature means clearly that the rotation motions can not be separed from the inversion.

Let us note that the isoenergetic inversion of methylamine may described by a fourth independent angle α followed by a simultaneous C_2 rotation of the methyl groups (8). This motion describes essentially the inversion of the three carbon atoms

Table 1
Character table for the triple equivalent rotation in planar trimethylamine. a_m, b_m, c_m and d_m symbolize the operations belonging to a certain class.

	1	6	6	2	6	6	18	36	27	54	9	18	18	18	18	27	54	
	a_0	a_1	a_2	a_4	a_3	a_5	a_6	a_7	b_1	b_2	c_1	c_3	c_2	c_4	c_5	d_1	d_2	
A_1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	z
A_2	1	1	1	1	1	1	1	1	1	1	−1	−1	−1	−1	−1	−1	−1	
E_1	2	2	2	2	2	2	−1	−1	2	−1	0	0	0	0	0	0	0	x, y
A_3	1	1	1	1	1	1	1	1	−1	−1	1	1	1	1	1	−1	−1	
A_4	1	1	1	1	1	1	1	1	−1	−1	−1	−1	−1	−1	−1	1	1	R_z
E_2	2	2	2	2	2	2	−1	−1	−2	1	0	0	0	0	0	0	0	R_x, R_y
I_1	6	3	0	−3	0	−3	0	0	0	0	2	−1	2	−1	−1	0	0	
I_2	6	3	0	−3	0	−3	0	0	0	0	−2	1	−2	1	1	0	0	
I_1'	6	0	0	6	−3	0	0	0	0	0	0	0	0	0	0	2	−1	
I_2'	6	0	0	6	−3	0	0	0	0	0	0	0	0	0	0	−2	1	
I_3'	6	0	−3	−3	0	3	0	0	0	0	2	2	−1	−1	−1	0	0	
I_4'	6	0	−3	−3	0	3	0	0	0	0	−2	−2	1	1	1	0	0	
E_1''	2	−1	−1	2	2	−1	2	−1	0	0	2	−1	−1	−1	2	0	0	
E_2''	2	−1	−1	2	2	−1	2	−1	0	0	−2	1	1	1	−2	0	0	
G	4	−2	−2	4	4	−2	−2	1	0	0	0	0	0	0	0	0	0	
I_1''	6	−3	3	−3	0	0	0	0	0	0	2	−1	−1	2	−1	0	0	
I_2''	6	−3	3	−3	0	0	0	0	0	0	−2	1	1	−2	1	0	0	

with respect to the molecular symmetry plane of planar trimethylamine and the rearrangement of the methyl group to have an isoenergetic conformation. The corresponding operation (8), $\widehat{I}$, is easily verified to commute with respect to the $\widehat{U}$ and $\widehat{V}$ operations of planar trimethylamine. It does not commute, however, with the G_{27} and W^I subgroup operations. Nevertheless, since the $\widehat{I}$ and $\widehat{U}$ operations do affect exacty in the same way the operations of both subgroups, it is easily seen that the product $\widehat{I} \times \widehat{U}$ commutes with all the operations of the planar trimethylamine group. As a result, a two-dimensional subgroup may be defined:

$$(IU)^I = \left[\widehat{E} + \widehat{I}\,\widehat{U}\right], \tag{25}$$

where the operation $\widehat{I} \times \widehat{U}$ only depends on the independent inversion angle α.

Finally, it is seen that the G_{648} r-NRG for pyramidal trimethylamine may be written as a direct product of the G_{324} of planar trimethylamine and the $(IU)^I$ subgroup:

$$G_{648} = \left[U^I \wedge W^I\right] \wedge \left[C^I_{3_1} \times C^I_{3_2} \times C^I_{3_3}\right] \times V^I \times (IU)^I. \tag{26}$$

Cosine or sine functions of the angle α will multiply each symmetry eigenvector of planar trimethylamine in order to form symmetric or antisymmetric vectors with respect to the $\widehat{I}\,\widehat{U}$ inversion operation. In particular, the potential energy hypersurface, which presents now 54 energy wells, will be described by the energy function of A_1 symmetry (24) multiplied by $\cos N\alpha$. Taking into account the degeneracies of the sublevels, these will exhibit a twelve-fofd near degenarate substructure.

5. Conclusions

The present character table for planar trimethylamine has been deduced from:

– the structure of the group:

$$G_{324} = \left[U^I \wedge W^I\right] \wedge \left[C^I_{3_1} \times C^I_{3_2} \times C^I_{3_3}\right] \times V^I; \tag{27}$$

– the division of the group in 17 classes, the sum of the square of the dimensions of which gives the order of the group:

$$4 \times (1)^2 + 4 \times (2)^2 + 1 \times (4)^2 + 8 \times (6)^2 = 324;$$

– the composition of the 17 classes in: 1, 6 , 6, 2, 6, 6, 18, 36, 27, 54, 9, 18, 18, 18, 18, 27 and 54 elements.

The orthogonality rules between the irreducible representations allow to write from the characters a system of 17 linear equations, the solutions of which are the dimensions of the classes.

It may be concluded that the character table for planar trimethylborane or trimethylamine is given by table 1.

It seen that the r-NRG for pyramidal trimethylamine is given as a direct product of the r-NRG for planar trimethylamine and the two-dimensional pyramidal $(IU)^I$ inversion group.

The potential energy function for the triple methyl rotation and inversion will be described by a 54-fold well potential energy hypersurface. As a result, the spectrum of trimethylamine is expected to possess 27×2 substates $(4I + 1E + 1A) \times 2$. Taking into account the degeneracies, the spectrum is expected to exhibit a sextet structure, each of sublevel of which is again formed by doublets. However, since the pyramidal barrier inversion is probably very high, the doublet substructure will be not easily detected. With such a result, the spectroscopists are invited to measure the FIR spectrum of trimethylamine.

The r-NRG groups appear to be more descriptive, i.e., informative than the MSG of Longuet-Higgins, and it seems to be advantageously used to study the internal dynamics of small organic molecules, such as trimethylamine, which possess a solid frame.

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