

The non-rigid group for wagging and torsion modes in methylamine

Yves G. Smeyers^a, Maria Villa^{a,b} and Elba Ortiz^b

^a *Instituto de Estructura de la Materia, CSIC, E-28006 Madrid, Spain*

^b *U.A.M.-I., Departamento de Química, Purísima y Michoacan S/N, CP09340, México, DF, México*

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The non-rigid group (NRG) for the wagging and torsion motions in methylamine is deduced in terms of rotation and inversion operations. The group is compared to that of Longuet-Higgins for the same molecule expressed in terms of permutations and permutations-inversion. It is seen that the NRG is isomorphic to that of Longuet-Higgins and the C_{6v} symmetry point group. The character table is deduced, as well as the symmetry eigenvectors in terms of products of trigonometric functions. Selection rules for the infrared torsional-wagging transitions are given, and the band profiles of the spectrum discussed.

1. Introduction

Methylamine ($\text{CH}_3\text{-NH}_2$) is well known as a typical example of a non-rigid molecule possessing two different types of large amplitude motions [1,2]. These two modes are the in phase wagging of the hydrogen atoms of the amine moiety, and the torsion of the methyl rest around the C–N bond. As is well known, these two large amplitude motions give rise to a fine structure in the vibrational states, because of a tunneling among six equivalent minima on the torsion-inversion potential energy surface [3,4].

The analysis of the vibrational state structure requires the use of the non-rigid group theory [5–8]. The non-rigid group for methylamine was given by Onashi et al. [6] in terms of permutation and permutation-inversion operations [5].

In the present paper, we shall develop the same group in terms of physical operations, i.e., rotations and inversions (NRG), which offer the advantage of an easier physical interpretation [8,9]. Notice that this point of view was initially introduced by Altmann in a previous theory [10], as well as by other authors [11].

2. Theory

For this purpose, let us consider methylamine, as in fig. 1, in which the rotation

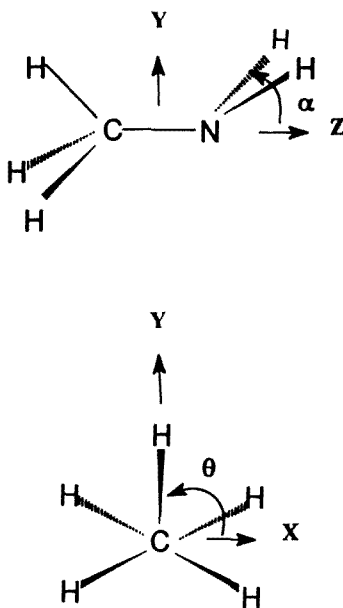


Fig. 1. Large amplitude motions in methylamine: wagging and torsion.

angle, θ , of the methyl moiety is defined counterclockwise from the ZX plane as origin, and the wagging angle of the amine group, α , defined in the same way when viewed from the molecular center. As a result, the Hamiltonian operator for the wagging and torsion in methylamine may be written as

$$H = -\frac{\partial}{\partial\theta} B_{\theta} \frac{\partial}{\partial\theta} - \frac{\partial}{\partial\theta} B_{\theta,\alpha} \frac{\partial}{\partial\alpha} - \frac{\partial}{\partial\alpha} B_{\alpha,\theta} \frac{\partial}{\partial\theta} - \frac{\partial}{\partial\alpha} B_{\alpha} \frac{\partial}{\partial\alpha} + V(\theta, \alpha), \quad (1)$$

where B_{θ} and B_{α} are the kinetic parameters, which depend to some extent on the wagging and torsion angles, $B_{\alpha,\theta}$ and $B_{\theta,\alpha}$ the kinetic coupling terms, and $V(\theta, \alpha)$ the potential energy operator.

In order to establish the non-rigid group (NRG) for the torsion and wagging in methylamine, let us consider that the Hamiltonian operator is invariant under the following operations:

- (1) a threefold rotation of the methyl moiety: $\hat{C}_3 F(\theta, \alpha) = F(\theta + 2\pi/3, \alpha)$;
- (2) a rotation of 180° followed by a sign change of the rotation angle:

$$\hat{U} F(\theta, \alpha) = F(\pi - \theta, \alpha);$$

- (3) a simultaneous sign change of both rotation and wagging angles;

$$\hat{V} F(\theta, \alpha) = F(-\theta, -\alpha).$$

These operations are illustrated in fig. 2. As a result, the non-rigid group for

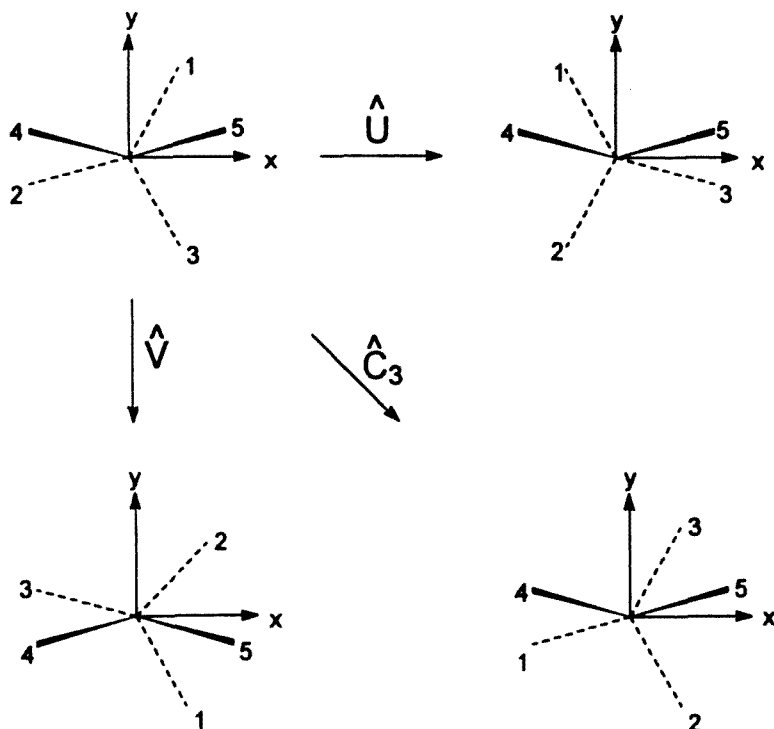


Fig. 2. The simple switch (\hat{U}), double switch (\hat{V}), three-fold rotation \hat{C}_3 operations in methylamine.

wagging and torsion in methylamine may be written as a product of three subgroups:

$$C_3^I \wedge [V^I \times U^I] = G_{12}, \quad (2)$$

which is a group of order twelve where

$$\begin{aligned} C_3^I &= [\hat{E} + \hat{C}_3 + \hat{C}_3^2], \\ V^I &= [\hat{E} + \hat{V}], \\ U^I &= [\hat{E} + \hat{U}]. \end{aligned} \quad (3)$$

From these operations the multiplication table can be easily deduced. It is given in table 1, where it can be seen that this group contains six classes of operations and six irreducible representations, i.e., the group is isomorphic with that of Longuet-Higgins and the C_{6v} symmetry point group. The character table is given in table 2.

The \hat{C}_3 , \hat{V} and \hat{U} physical operations are the basic operations of the group. However, they are not necessarily the generators of the group. These generators can be easily constructed taking into account the isomorphism with the C_{6v} symmetry

Table 1
Multiplication table ^a.

	<i>E</i>	<i>C</i> ₃	<i>C</i> ₃ ²	<i>VUC</i> ₃	<i>VUC</i> ₃ ²	<i>UV</i>	<i>V</i>	<i>VC</i> ₃	<i>VC</i> ₃ ²	<i>U</i>	<i>UC</i> ₃	<i>UC</i> ₃ ²
<i>E</i>	<i>E</i>	<i>C</i> ₃	<i>C</i> ₃ ²	<i>VUC</i> ₃	<i>VUC</i> ₃ ²	<i>UV</i>	<i>V</i>	<i>VC</i> ₃	<i>VC</i> ₃ ²	<i>U</i>	<i>UC</i> ₃	<i>UC</i> ₃ ²
<i>C</i> ₃	<i>C</i> ₃	<i>C</i> ₃ ²	<i>E</i>	<i>VUC</i> ₃ ²	<i>UV</i>	<i>VUC</i> ₃	<i>VC</i> ₃ ²	<i>V</i>	<i>VC</i> ₃	<i>UC</i> ₃ ²	<i>U</i>	<i>UC</i> ₃
<i>C</i> ₃ ²	<i>C</i> ₃ ²	<i>E</i>	<i>C</i> ₃	<i>UV</i>	<i>VUC</i> ₃	<i>VUC</i> ₃ ²	<i>VC</i> ₃	<i>VC</i> ₃ ²	<i>V</i>	<i>UC</i> ₃	<i>UC</i> ₃ ²	<i>U</i>
<i>VUC</i> ₃	<i>VUC</i> ₃	<i>VUC</i> ₃ ²	<i>UV</i>	<i>C</i> ₃ ²	<i>E</i>	<i>C</i> ₃	<i>UC</i> ₃ ²	<i>U</i>	<i>UC</i> ₃	<i>VC</i> ₃ ²	<i>V</i>	<i>VC</i> ₃
<i>VUC</i> ₃ ²	<i>VUC</i> ₃ ²	<i>UV</i>	<i>VUC</i> ₃	<i>E</i>	<i>C</i> ₃	<i>C</i> ₃ ²	<i>UC</i> ₃	<i>UC</i> ₃ ²	<i>U</i>	<i>VC</i> ₃	<i>VC</i> ₃ ²	<i>V</i>
<i>UV</i>	<i>UV</i>	<i>VUC</i> ₃	<i>VUC</i> ₃ ²	<i>C</i> ₃	<i>C</i> ₃ ²	<i>E</i>	<i>U</i>	<i>UC</i> ₃	<i>UC</i> ₃ ²	<i>V</i>	<i>VC</i> ₃	<i>VC</i> ₃ ²
<i>V</i>	<i>V</i>	<i>VC</i> ₃	<i>VC</i> ₃ ²	<i>UC</i> ₃	<i>UC</i> ₃ ²	<i>U</i>	<i>E</i>	<i>C</i> ₃	<i>C</i> ₃ ²	<i>UV</i>	<i>VUC</i> ₃	<i>VUC</i> ₃ ²
<i>VC</i> ₃	<i>VC</i> ₃	<i>VC</i> ₃ ²	<i>V</i>	<i>UC</i> ₃ ²	<i>U</i>	<i>UC</i> ₃	<i>C</i> ₃ ²	<i>E</i>	<i>C</i> ₃	<i>VUC</i> ₃ ²	<i>UV</i>	<i>VUC</i> ₃
<i>VC</i> ₃ ²	<i>VC</i> ₃ ²	<i>V</i>	<i>VC</i> ₃	<i>U</i>	<i>UC</i> ₃	<i>UC</i> ₃ ²	<i>C</i> ₃	<i>C</i> ₃ ²	<i>E</i>	<i>VUC</i> ₃	<i>VUC</i> ₃ ²	<i>UV</i>
<i>U</i>	<i>U</i>	<i>UC</i> ₃	<i>UC</i> ₃ ²	<i>VC</i> ₃	<i>VC</i> ₃ ²	<i>V</i>	<i>UV</i>	<i>VUC</i> ₃	<i>VUC</i> ₃ ²	<i>E</i>	<i>C</i> ₃	<i>C</i> ₃ ²
<i>UC</i> ₃	<i>UC</i> ₃	<i>UC</i> ₃ ²	<i>U</i>	<i>VC</i> ₃ ²	<i>V</i>	<i>VC</i> ₃	<i>VUC</i> ₃ ²	<i>UV</i>	<i>VUC</i> ₃	<i>C</i> ₃ ²	<i>E</i>	<i>C</i> ₃
<i>UC</i> ₃ ²	<i>UC</i> ₃ ²	<i>U</i>	<i>UC</i> ₃	<i>V</i>	<i>VC</i> ₃	<i>VC</i> ₃ ²	<i>VUC</i> ₃	<i>VUC</i> ₃ ²	<i>UV</i>	<i>C</i> ₃	<i>C</i> ₃ ²	<i>E</i>

^a For the sake of simplicity, the operator symbol has been omitted.

point group. These can be any product of the \hat{C}_3 operation by an operation of one of the subgroups of order two. For example: $\hat{C}_3\hat{V}$ and \hat{U} .

These operations have their equivalents in the permutation and permutation-inversion formalism of Longuet-Higgins [5]. They are given next:

$$\begin{aligned} \hat{E} &= (1), & \hat{U} &= (23)(45)^*, \\ \hat{C}_3 &= (123), & \hat{U}\hat{C}_3 &= (31)(45)^*, \\ \hat{C}_3^2 &= (132), & \hat{U}\hat{C}_3^2 &= (12)(45)^*, \\ \hat{V} &= (23)^*, & \hat{U}\hat{V} &= (45), \\ \hat{V}\hat{C}_3 &= (31)^*, & \hat{U}\hat{V}\hat{C}_3 &= (123)(45), \\ \hat{V}\hat{C}_3^2 &= (12)^*, & \hat{U}\hat{V}\hat{C}_3^2 &= (132)(45). \end{aligned}$$

Table 2
Character table G_{12} .

	\hat{E}	$2\hat{C}_3$	$2\hat{U}\hat{V}\hat{C}_3$	$\hat{U}\hat{V}$	$3\hat{V}\hat{C}_3$	$3\hat{U}\hat{C}_3$
<i>A</i> ₁	1	1	1	1	1	1
<i>A</i> ₂	1	1	1	1	-1	-1
<i>B</i> ₁	1	1	-1	-1	1	-1
<i>B</i> ₂	1	1	-1	-1	-1	1
<i>E</i> ₁	2	-1	1	-2	0	0
<i>E</i> ₂	2	-1	-1	2	0	0

It is interesting to point out that the G_{12} non-rigid group for methylamine is identical to the C_{6v} symmetry point group, when expressed in the formalism of the permutation and permutation-inversion. On the contrary, these two groups are different, although isomorphic, when expressed in terms of physical operations.

3. Applications

3.1. THE SYMMETRY EIGENVECTORS

In order to simplify the solution of the Schrödinger equation for the Hamiltonian operator (1), as well as to classify the eigenvalues and eigenvectors, it is interesting to develop the solutions on the basis of the symmetry eigenvectors. These may be expressed in terms of products of trigonometric functions of the wagging and torsion angles, the integration of which is straightforward. These symmetry eigenvectors will diagonalize the Hamiltonian matrix into eight boxes.

From the character table, the following symmetry eigenvectors can be deduced:

$$\begin{aligned}
 A_1 & \begin{cases} \cos 3K\theta \cos L\alpha & \text{for } K = \text{even}, \\ \sin 3K\theta \sin L\alpha & \text{for } K = \text{odd}; \end{cases} \\
 A_2 & \begin{cases} \sin 3K\theta \cos L\alpha & \text{for } K = \text{even}, \\ \cos 3K\theta \sin L\alpha & \text{for } K = \text{odd}; \end{cases} \\
 B_1 & \begin{cases} \sin 3K\theta \sin L\alpha & \text{for } K = \text{even}, \\ \cos 3K\theta \cos L\alpha & \text{for } K = \text{odd}; \end{cases} \\
 B_2 & \begin{cases} \cos 3K\theta \sin L\alpha & \text{for } K = \text{even}, \\ \sin 3K\theta \cos L\alpha & \text{for } K = \text{odd}; \end{cases} \\
 E_1 & \begin{cases} \begin{cases} \sin(3K \pm 1)\theta \cos L\alpha & \text{for } K = \text{even}, \\ \cos(3K \pm 1)\theta \sin L\alpha & \text{for } K = \text{odd}, \end{cases} \\ \begin{cases} \cos(3K \pm 1)\theta \cos L\alpha & \text{for } K = \text{even}, \\ \sin(3K \pm 1)\theta \sin L\alpha & \text{for } K = \text{odd}; \end{cases} \end{cases} \\
 E_2 & \begin{cases} \begin{cases} \sin(3K \pm 1)\theta \sin L\alpha & \text{for } K = \text{even}, \\ \cos(3K \pm 1)\theta \cos L\alpha & \text{for } K = \text{odd}, \end{cases} \\ \begin{cases} \cos(3K \pm 1)\theta \sin L\alpha & \text{for } K = \text{even}, \\ \sin(3K \pm 1)\theta \cos L\alpha & \text{for } K = \text{odd}. \end{cases} \end{cases} \tag{4}
 \end{aligned}$$

The potential energy operator of expression (1) will be totally symmetric. As a result, it may be developed on the basis of the eigenvectors of symmetry A_1 :

$$V(\theta, \alpha) = \sum_{K=\text{even}, L} A_{KL} \cos 3K\theta \cos L\alpha + \sum_{K=\text{odd}, L} B_{KL} \sin 3K\theta \sin L\alpha. \quad (5)$$

In the same way, the kinetic parameters and coupling terms of (1) may be developed in terms of A_1 vectors.

The potential energy coefficients of (5) may be determined by a least-square fitting of a set of previously determined energy values in an electronic ab initio calculation for different conformations. In the same way, the kinetic parameters can be determined from the optimal geometries. The energy levels and torsional-wagging functions are then determined by diagonalization of the factorized Hamiltonian matrix expanded in terms of the symmetry eigenvectors (4).

3.2. SELECTION RULES FOR THE INFRARED SPECTRUM

As is well known, the far-infrared intensities are given by the electric dipole moment variation with respect to the transition. The question is to know under which symmetry operations of the G_{12} group, each dipole moment component remains invariant. It is clear that these components retain the threefold symmetry of the methyl moiety [12]. As a result, only the \hat{V} , \hat{U} and $\hat{V}\hat{U}$ have to be considered. From the non-rigid group, G_4 , isomorphic with the symmetry point group, C_{2v} , it may be easily seen that the Z , X and Y components transform according to the A_1 , B_1 and B_2 irreducible representations of G_{12} , respectively.

From these symmetry properties, as well as from the character table, the selection rules for the vibrational transitions are easily deduced. They are given in table 3.

3.3. BAND PROFILES

In order to establish the FIR band profiles we need to know the mean values of the principal moments of inertia, as well as their relative orientation with respect to that of the dipole moment variations. In methylamine both orientations are roughly coincident, the mean values of principal moments of inertia are: $I_y = 21.5$,

Table 3
Selection rules.

μ_z	μ_x	μ_y
$A_1 \rightarrow A_1$	$A_1 \rightarrow B_1$	$A_1 \rightarrow B_2$
$A_2 \rightarrow A_2$	—	—
$B_1 \rightarrow B_1$	$B_1 \rightarrow A_1$	—
$B_2 \rightarrow B_2$	—	$B_2 \rightarrow A_1$
$E_1 \rightarrow E_1$	$E_1 \rightarrow E_2$	$E_1 \rightarrow E_2$
$E_2 \rightarrow E_2$	$E_2 \rightarrow E_1$	$E_2 \rightarrow E_1$

$I_x = 20.0$ and $I_z = 7.5$ UAM \AA^2 , i.e., methylamine appears to be a nearly prolate symmetric top.

The most relevant dipole moment variations, which correspond to the wagging mode, take place along the Z and Y axes. These give rise to A and C type band progressions, respectively. The dipole moment variation corresponding to the torsion mode is parallel to the X axis. This gives rise to the B type band system, probably too weak to be observed.

Since methylamine is nearly a prolate symmetrical top, the selection rules for the external rotation are $\Delta J = \pm 1$ and $\Delta K = \pm 1$ for $K_a = 0$, and $\Delta J = 0, \pm 1$ and $\Delta K = \pm 1$ for $K_a \neq 0$. In the same way, the selection rules for a C type band are $\Delta J = 0, \pm 1$ and $\Delta K = \pm 1$ for $K_c = \pm 1$ [13].

Taking into account that methylamine is a relatively small molecule, i.e., the values of the principal moments of inertia are relatively small, a broad rotational structure can be expected. As a result, the transitions along the Z axis would give rise to A type band with a sharp Q branch, whereas those along the Y axis would give rise to a broad structure with P, Q and R branches. The wagging mode is expected to give the most intense transitions.

3.4. NUCLEAR STATISTICAL WEIGHTS

As is well known, the wave-function, ψ_N , that describes the motion of the nuclei has to be completely symmetric or antisymmetric with respect to the interchanging of the position or spin coordinates of all identical particles [14]. In the case of an internal motion, the overall rotation and spin nuclear functions, ψ_R and ψ_S have also to be taken into account:

$$\psi_N = \psi_V \psi_R \psi_S, \quad (6)$$

where ψ_V is the large amplitude motion wave-function.

The symmetry properties of the rotation-wagging wave-function of methylamine are given by the non-rigid group G_{12} (2). In the case of a band of type A or C, the overall rotation functions can be only completely symmetric or antisymmetric. Furthermore, since we are not interested in the individual rotational lines, but rather in the overall torsional band contours, only an average weight has to be retained. As a result, the $\psi_V \times \psi_S$ products have to be only completely symmetric or antisymmetric.

When the two possible spin coordinates of the hydrogen atoms, and the three possible ones of deuteriums, are taken into account, the spin nuclear wave-functions can exhibit degeneracies of order $2^5 = 32$, or $3^5 = 243$, respectively. All these functions can be classified according to the irreducible representation of the non-rigid group G_6 , a set analogous to the G_{12} group, in which the double switch operation, \hat{V} , has been deleted. The spin wave-functions behave indeed as vectors and no symmetry plane can be retained.

The degeneracies, or nuclear statistical weights, are then given, for each

wagging-torsional symmetry, by the number of completely symmetric or antisymmetric components in all the possible products $\psi_V \psi_S$. In methylamine h_5 , we found 16 and 16, completely symmetric or antisymmetric products for the *A* and *E* representations, and in methylamine d_5 , 99 and 144. That means that *E–E* and *A–A* transitions will have the same nuclear statistical weight in methylamine h_5 , and in methylamine d_5 the *E–E* transitions will be 3/2 times larger than the *A–A* ones.

4. Conclusions

Because methylamine is a relatively small molecule, and because of its prolate nature, it may be expected that the FIR spectrum of this molecule would present *A* type band progressions with sharp *Q* branches and *C* type ones with *P*, *Q* and *R* branches. These features would give rise to a very congested structure, in which the fine torsional substructure would likely not be easily distinguishable. The transitions corresponding to the wagging mode are expected to be the most intense.

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