

On the normal vibrations of nonrigid molecule $B(CH_3)_3$

T S G KRISHNA MURTY, L S R K PRASAD and
M KONDALA RAO

Applied Mathematics Department, Andhra University, Waltair 530 003, India

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Abstract. Treating the symmetry operations as transformations in higher dimensional space, it is shown that Wigner's method can be straightaway extended to study the vibrations of nonrigid molecules exhibiting free or nearly free internal rotations. The molecule $B(CH_3)_3$ is illustrated.

Keywords. Isodynamic operation; symmetry group; symmetry coordinates; normal vibrations; non-rigid molecule.

1. Introduction

A complete analysis of the normal modes of oscillation of a molecule would be of great help in interpreting the Raman and infrared spectra. Wigner (1930) showed how group theory could be used effectively towards this end. Subsequently Tisza (1933), Wilson (1934), Placzek (1934), Rosenthal and Murphy (1936) made important contributions to the subject. Wilson (1934) applied Wigner's (1930) method to the benzene molecule and obtained its normal modes and frequencies. Rosenthal and Murphy (1936) made a detailed report on the subject—with the required elements of group theory and their representations—and showed the utility of the group theoretical method in solving the problem of molecular vibrations of polyatomic molecules. Later, the normal modes and frequencies of the sulphur molecule were worked out by Bhagavantam and Venkatarayudu (1938) using the same method. There has been much interest recently in the vibrations of nonrigid molecules which exhibit free or nearly free internal rotation (Hougen 1964; Bunker 1965; Fleming and Banwell 1969). Some of these studies suggest the possibility of extending Wigner's method to the case of nonrigid molecules also. In the present paper, the possibility of extending Wigner's group theoretical method to the problem of normal vibrations of the nonrigid molecule $B(CH_3)_3$ is studied and the selection rules for the Raman and infrared spectra of this molecule are worked out. The number of modes active in the infrared spectra agrees with the corresponding number experimentally reported by Stewart (1956).

2. Method of extension

Longuet-Higgins (1963) and Altmann (1967, 1971, 1977) obtained, in two different ways, the symmetry groups of nonrigid molecules with free or nearly free internal

rotations. There has been a good deal of discussion (Watson 1971), Longuet-Higgins 1978, 1979; Krishna Murthy *et al* 1980 over the equivalence of the groups obtained by the two authors. For the present, we take the symmetry group, its character table and the diagrammatic representation of the molecule $B(\text{CH}_3)_3$ from Altmann (1977).

The model assumed for the molecule contains a rigid frame consisting of a boron atom and the three carbon atoms, and the three methyl groups rotating freely and independently about the three BC bonds (figure 20.6-1 of Altmann 1977). Through the introduction of isodynamic operations, Altmann (1977) obtained the symmetry group of this molecule in the form of a semi-direct product— $G' = (C'_{31} \otimes C'_{32} \otimes C'_{33}) \wedge D'_{3h}$. The symmetry operation R of this group is not simply a rotation or a rotation-reflection of the molecule as a whole, as in the case of rigid molecules. Instead, it is a composite one—the product of an operation from the group D'_{3h} , known as the group of molecular constraints and an operation from the group $(C'_{31} \otimes C'_{32} \otimes C'_{33})$, known as intrinsic group. The orientation of a methyl group relative to the rigid frame is given by the intrinsic angle τ . Usually, an equilibrium configuration of the molecule is fully known when the coordinates of the atoms of the molecule relative to the three space fixed axes (in other words, the three space coordinates of all the atoms of the molecule) are given. However, all the symmetry operations of this molecule cannot be described by a change in these three coordinates only. For instance, under the isodynamic rotation C'_{31} , the coordinates of all but three atoms remain invariant. Whatever be the choice of axes, it is not possible to find a linear transformation in this three-dimensional space that completely represents the symmetry operation. Thus, six more coordinates corresponding to the three intrinsic angles are introduced here so that every symmetry operation can be described as a linear transformation in this 9-dimensional space. One is led to consider the 9-dimensional space from the way the symmetry group of this molecule has been constructed by Altmann (1977.) This implies that, as far as the physical motion of the atoms of the molecule is concerned, the last six coordinates need suitably be interpreted taking the physics of the molecule into consideration. Now, all the operations of the symmetry group can be realised, as linear transformations, in the space constituted by a set of the three right-handed systems:

- (i) X_{11}, X_{12}, X_{13} (chosen to be parallel to the space fixed axes) with B as origin and BC_1 bond as X_{12} axis.
- (ii) X_{21}, X_{22}, X_{23} with B as origin and BC_2 bond as X_{22} axis
- (iii) X_{31}, X_{32}, X_{33} with B as origin and BC_3 bond as X_{32} axis.

The space coordinate axes X, Y, Z are fixed with B as origin and BC_1 bond as Y -axis.

Now, the matrices representing the generators of the symmetry group of the molecule are given by

$$C_3^+ : \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \quad \sigma_h : \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 \end{bmatrix}$$

$$\sigma_{v_1} : \begin{bmatrix} -1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 \end{bmatrix} \quad C_{31}^+ : \begin{bmatrix} -\frac{1}{2} & 0 & \frac{\sqrt{3}}{2} & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ -\frac{\sqrt{3}}{2} & 0 & -\frac{1}{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

$$C_{32}^+ : \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & -\frac{1}{2} & 0 & \frac{\sqrt{3}}{2} & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & \frac{\sqrt{3}}{2} & 0 & -\frac{1}{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \quad C_{33}^+ : \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & -\frac{1}{2} & 0 & \frac{\sqrt{3}}{2} \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & \frac{\sqrt{3}}{2} & 0 & -\frac{1}{2} \end{bmatrix}$$

The above matrices clearly describe the operations under consideration. For instance, consider the isodynamic rotation C'_2 (Altmann 1977). Its matrix representation is described by

$$\begin{array}{cccccc|cccc} -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 \\ \hline 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 \\ \hline 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 \end{array}$$

For convenience, we relabel the 9 coordinates as (x_1, x_2, \dots, x_9) instead of $(x_{11}, x_{12}, \dots, x_{32}, x_{33})$. It can easily be seen that the matrix completely describes the effect of the operation on the position of the atoms of the molecule in space. The effect on the intrinsic angles (Altmann 1977) can be seen thus:

$$\begin{aligned} \tan \tau'_1 &= \frac{x'_3}{x'_1} = \frac{-x_3}{-x_1} = \frac{-x_3/(x_1^2 + x_3^2)^{1/2}}{-x_1/(x_1^2 + x_3^2)^{1/2}} = \frac{-\sin \tau_1}{-\cos \tau_1} = \frac{\sin(\pi + \tau_1)}{\cos(\pi + \tau_1)} \\ &= \tan(\pi + \tau_1); \text{ therefore } \tau'_1 = \pi + \tau_1 \end{aligned}$$

$$\begin{aligned} \tan \tau'_2 &= \frac{x'_6}{x'_4} = \frac{-x_6}{-x_7} = \frac{-x_6/(x_4^2 + x_6^2)^{1/2}}{-x_7/(x_4^2 + x_6^2)^{1/2}} = \frac{-\sin \tau_3}{-\cos \tau_3} = \frac{\sin(\pi + \tau_3)}{\cos(\pi + \tau_3)} \\ &= \tan(\pi + \tau_3); \text{ therefore } \tau'_2 = \pi + \tau_3. \end{aligned}$$

$$\begin{aligned} \text{Similarly, } \tan \tau'_3 &= \frac{x'_9}{x'_7} = \frac{-x_8}{-x_4} = \frac{-x_8/(x_4^2 + x_8^2)^{1/2}}{-x_4/(x_4^2 + x_8^2)^{1/2}} = \frac{-\sin \tau_2}{-\cos \tau_2} = \frac{\sin(\pi + \tau_2)}{\cos(\pi + \tau_2)} \\ &= \tan(\pi + \tau_2); \text{ therefore } \tau'_3 = \pi + \tau_2. \end{aligned}$$

When a system of axes, parallel to the one described above, is introduced at the equilibrium position of each atom of the molecule, the dynamical system *i.e.*, the molecule could completely be defined by the $9n$ coordinates, where n is the number of atoms of the molecule (in this case $n=13$). So all the symmetry coordinates may be expressed as linear functions of $9n$ coordinates. Note here that though a 9-dimensional picture is considered for the purpose of extension of Wigner's method, final results are to be interpreted appropriately. For instance, if a symmetry coordinate transforming according to the identity representation, is found to be, say

$$\begin{aligned} S &= (x_5^6 + x_9^6) + (x_6^7 + x_3^7) + (x_2^9 + x_8^9) + (x_2^{10} + x_8^{10}) \\ &\quad + (x_2^{12} + x_8^{12}) + (x_2^{13} + x_8^{13}), \end{aligned}$$

where x_j^i stands for a unit displacement of the i th atom in the j th direction. Now we interpret that in this vibrational state the displacement of the 6th atom is given by the resultant, both in magnitude and direction, of a unit displacement in 5th as well as 8th directions. For the displacements of the other atoms also, similar interpretation holds.

Following the treatment of Bhagavantham and Venkatarayudu (1969) the exact matrices, in the reducible representation defined by the $9n$ coordinates, corresponding to the generators of the symmetry group can easily be found. But, as required for the present discussion, only the character $\chi_\rho(R)$, in this reducible representation, of each of the operation R is found and tabulated (table 1). Using the Frobenius (1896) formula

$$n_i = \frac{1}{N} \sum_{\rho} h_{\rho} \chi_{\rho}(R) \chi_i(R), \quad (1)$$

where N is the order of the group $\chi_{\rho}(R)$, is the compound character found above and $\chi_i(R)$ is the character of the i th irreducible representation of the group, the number of normal modes n_i appearing against each irreducible representation of the group is found and tabulated (table 1).

The character $\chi_{\rho}^t(R)$ arising from the normal coordinates corresponding to translations and $\chi_{\rho}^r(R)$ arising from the normal coordinates corresponding to the rotations are found and tabulated (table 1). The character $\psi_{\rho}(R)$ of any operation R in the representation defined by the normal coordinates excluding translations and rotations is found by subtracting $\chi_{\rho}^t(R)$ and $\chi_{\rho}^r(R)$ from $\chi_{\rho}(R)$ and tabulated (table 1). Again, using formula (1) with $\psi_{\rho}(R)$ in place of $\chi_{\rho}(R)$, n'_i , the number of normal modes excluding translations and rotations, appearing against each irreducible representation is found and tabulated (table 1).

3. Selection rules

The character $\chi_{\rho}^I(R)$ of any operation R in the reducible representation defined by the linear combinations of the components of the electric moment vector is found and tabulated (table 1). The normal coordinates coming under any irreducible representation are classified as active or inactive in infrared absorption according as

$$n_i = \frac{1}{N} \sum_{\rho} h_{\rho} \chi_{\rho}^I(R) \chi_i(R)$$

is nonzero or zero. The results are presented in table 1.

Similarly, the character $\chi_{\rho}^R(R)$ of any operation R in the reducible representation defined by the linear combinations of the components of the polarisability tensor is found and tabulated (table 1). The normal coordinates coming under any irreducible representation are classified as active or inactive in Raman scattering according as

$$n_i = \frac{1}{N} \sum_{\rho} h_{\rho} \chi_{\rho}^R(R) \chi_i(R),$$

is nonzero or zero. The results are presented in table 1.

Table 1. Characters of the irreducible representations of $(C_{31} \otimes C_{32} \otimes C_{33}) \wedge D_{3h}^1$

Class	E (000)	E (011)	E (012)	E (111)	E (112)	E (12)	E_3^+ (000)	C_3^+ (001)	C_3^+ (000)	C_{21} (001)	C_{21} (100)	C_{21} (101)	C_{21} (111)	σ_h (000)	σ_h (000)	S_8^+ (000)	σ_{v_1} (000)	σ_{v_1} (000)	σ_{v_1} (000)	n_i	n_i	n_i	Infra-Raman red	
Order	1	6	6	6	6	6	18	36	9	18	18	18	18	27	27	54	27	54	27	54				
Rep	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	7	6	A	A
(000) A_1'	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	3	3	A	A
(000) A_2'	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	2	1	f	f
(000) A_1''	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	2	1	f	f
(000) A_2''	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	f	f
(000) E'	2	2	2	2	2	2	-1	-1	0	0	0	0	0	2	-1	0	0	0	0	10	9	9	A	A
(000) E''	2	2	2	2	2	2	-1	-1	0	0	0	0	0	2	-1	0	0	0	0	3	2	2	f	f
(001) A	6	3	0	0	-3	-3	0	0	2	2	-1	-1	-1	0	0	0	0	0	0	4	4	4	f	A
(001) B	6	3	0	0	-3	-3	0	0	-2	-2	1	1	1	0	0	0	0	0	0	9	7	7	A	A
(011) A	6	0	-3	0	-3	3	0	0	2	-1	2	-1	-1	0	0	0	0	0	0	0	0	0	—	—
(011) B	6	0	-3	0	-3	3	0	0	-2	1	-2	1	1	0	0	0	0	0	0	0	0	0	—	—
(012) A'	6	0	0	-3	6	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	—	—
(012) A''	6	0	0	-3	6	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	—	—
(111) A_1	2	-1	-1	2	2	-1	2	-1	2	-1	-1	-1	2	0	0	0	0	0	0	0	0	0	—	—
(111) A_2	2	-1	-1	2	2	-1	2	-1	2	-1	1	1	-2	0	0	0	0	0	0	0	0	0	—	—
(111) E	4	-2	-2	4	4	-2	-2	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	—	—
(112) A	6	-3	-3	0	-3	0	0	0	2	-1	-1	2	-2	0	0	0	0	0	0	0	0	0	—	—
(112) B	6	-3	-3	0	-3	0	0	0	-2	1	1	-2	1	0	0	0	0	0	0	0	0	0	—	—
$x_p(R)$	117	78	39	39	0	0	0	0	-5	-5	10	10	10	21	0	3	3							
$x_p^t(R)$	9	6	3	3	0	0	0	0	-1	-1	2	2	2	3	0	1	1							
$x_p^r(R)$	9	6	3	3	0	0	0	0	-1	-1	2	2	2	-3	0	-1	-1							
$\phi_p(R)$	99	66	33	33	0	0	0	0	-3	-3	6	6	6	21	0	3	3							
$x_p^l(R)$	9	6	3	3	0	0	0	0	-1	-1	2	2	2	3	0	1	1							
$x_p^R(R)$	45	21	6	6	0	0	0	0	5	2	5	2	2	9	0	5	2							

Following the procedure adopted by Bhagavantam and Venkatarayudu (1938) to obtain the symmetry coordinates of sulphur molecule, the symmetry coordinates of this molecule $B(CH_3)_3$ can be derived. Use of little group technique (Krishna Murty *et al* 1978) reduces labour in obtaining the symmetry coordinates. Studies on the derivation of the symmetry coordinates of this molecule are under progress and will be reported separately.

4. Conclusion

The possibility of extending the Wigner's group theoretical method to the study of normal vibrations of nonrigid molecule $B(CH_3)_3$ is explored. Motivated by the description of the symmetry group of the molecule (Altmann 1977), the symmetry operations are realised in a suitable 9-dimensional space to facilitate the extension. The selection rules for fundamental lines in infrared absorption and Raman scattering are given. The number of modes that are active in infrared absorption is found to be 22 which is in good agreement with the experimental result reported by Stewart (1956). One may see that the dimensionality of the space in which Wigner's method can be extended is $2m+3$, where m is the number of freely moving methyl groups attached to a three-dimensional rigid frame.

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