

Symmetry coordinates of nonrigid molecules

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Abstract. Motivated by Altmann's definition of symmetry groups of nonrigid molecules, Wigner's method of obtaining the symmetry coordinates of a molecule is extended to nonrigid molecules with free internal rotations. The molecule BF_2CH_3 is exemplified.

Keywords. Nonrigid molecules; normal vibrations; vibrational symmetry coordinates; little group technique.

1. Introduction

In order to carry out the quantum mechanical treatment of molecular vibrations, it is necessary to find the normal coordinates coming under various irreducible representations (IRs) of the symmetry group of the molecule. Wigner (1930) applied group theory to obtain the normal coordinates of a molecule in an elegant way. Wigner's method has been successfully applied by many authors—for instance, Wilson (1934) to obtain the symmetry coordinates of benzene molecule and later Bhagavantham and Venkatarayudu (1938) to obtain those of sulphur molecule.

The problem of finding the symmetry coordinates in the case of nonrigid molecules is complex and the usual methods (Wilson *et al* 1955) do not seem to be quite suitable in this case.

During the past few decades, several authors worked in this area. One of the earlier studies is that of Crawford and Wilson (1941) who considered molecules having freely rotating symmetric tops and have shown that it is possible to find a set of coordinates (which are termed as internal symmetry coordinates) in terms of which both potential and kinetic energies of vibrations are independent of τ . Further, they have shown that the normal coordinates which are linear combinations of these internal symmetry coordinates will also be independent of τ 's. Hougen (1965, 1966) studied the obtention of normal coordinates of molecules which may exhibit free or nearly free internal rotations. Bunker (1967) obtained the symmetry coordinates of dimethyl acetylene by choosing the orthogonal combination of internal coordinate changes in a particular way. Later, Fleming and Banwell (1969) determined the vibrational states of nitromethane like molecules, which depend parametrically on the internal angle τ . They obtained the symmetry coordinates in terms of internal coordinates by a method which is essentially the same as that of Crawford and Wilson (1941).

In this paper, it will be shown how Altmann's (1977) definition of symmetry groups of nonrigid molecules with free internal rotations facilitates the extension of Wigner's method to determine the symmetry coordinates of such nonrigid molecules also. The method of extension will be exemplified through the molecule BF_2CH_3 .

In § 2, we apply the extension of Wigner's (1930) method (Krishna Murty *et al* 1980, hereafter referred to as paper I) for the vibrational analysis of the BF_2CH_3 molecule for the sake of completeness. A brief outline of Wigner's (1930) method of obtaining symmetry coordinates along with its extension to nonrigid molecules is given in § 3. In § 4, Wigner's method is extended to determine the symmetry coordinates of BF_2CH_3 . The results obtained are presented in § 5.

2. Vibrational analysis of BF_2CH_3

The model assumed for the molecule contains a rigid frame consisting of a boron atom, two fluorine atoms, a carbon atom and a freely rotating methyl group (figure 20·5-1 Altmann 1977). The symmetry group of the molecule as given by Altmann (1977) is $G' = C'_3 \otimes C'_{2v}$ and its character table is given in table 1.

As in paper I, we realise the symmetry operations of BF_2CH_3 molecule in a suitable 5-dimensional space. It may be noted that the 5-dimensional space can be obtained from the 9-dimensional space considered in paper I for $\text{B}(\text{CH}_3)_3$, by ignoring the coordinate axes X_{21} , X_{23} and X_{31} , X_{33} since the molecule BF_2CH_3 has only one rotating methyl group and each rotating methyl group requires two additional coordinates—in addition to the three space coordinates—to specify its orientation relative to the frame. The 5-dimensional space may thus be considered to be constituted:

Table 1. Characters of the irreducible representations of $C'_3 \otimes C'_{2v}$.

Rep	E	$2C'_3$	C_2	$2C_2C'_3$	$3\sigma_{v_1}$	$3\sigma_{v_2}$	n_l	n'_l	Infra-red	Raman
A'_1	1	1	1	1	1	1	11	9	A	A
A'_2	1	1	1	1	-1	-1	2	1	f	f
A''_1	1	1	-1	-1	1	-1	7	6	A	A
A''_2	1	1	-1	-1	-1	1	1	1	f	f
E'	2	-1	2	-1	0	0	1	1	f	A
E''	2	-1	-2	1	0	0	6	4	A	A
$\chi(R)$	35	14	-5	10	15	3				
$\chi^+(R)$	5	2	-1	2	3	1				
$\chi^-(R)$	3	0	-1	2	-1	-1				
$\psi(R)$	27	12	-3	6	13	3				
$\chi^I(R)$	5	2	-1	2	3	1				
$\chi^R(R)$	15	3	3	3	7	3				

(i) X_{11}, X_{12}, X_{13} (chosen to be parallel to the space fixed axes) with B as origin and BC bond as X_{12} axis.

*(ii) X_{21}, X_{22}, X_{23} With B as origin and BF_1 bond as X_{22} axis.

*(iii) X_{31}, X_{32}, X_{33} With B as origin and BF_2 bond as X_{32} axis.

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

The matrices representing the generators of the symmetry group $G' = C_3' \otimes C_{2v}'$ are:

$$c_3^+ : \begin{bmatrix} -1/2 & 0 & \sqrt{3}/2 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ -\sqrt{3}/2 & 0 & -1/2 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}; \quad c_2 : \begin{bmatrix} -1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 \end{bmatrix};$$

$$\sigma v_1 : \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}.$$

As in paper I, it may be seen that these matrices clearly describe the symmetry operations under consideration. For the sake of convenience, the five coordinates $x_{11}, x_{12}, x_{13}, x_{22}, x_{32}$ are relabelled as x_1, x_2, x_3, x_4, x_5 respectively.

Now, following the extension presented in paper I, the character $\chi(R)$ in the reducible representation defined by the $5n(n=7)$ coordinates is found and tabulated (table 1). The characters $\chi'(R)$ and $\chi''(R)$ arising from the normal modes corresponding respectively, to translations and rotations are also found and tabulated (table 1). The character $\psi(R)$ obtained by subtracting $\chi'(R)$ and $\chi''(R)$ from $\chi(R)$ is calculated and given in table 1. Using Frobenius formula, the number of normal modes including translations and rotations n_i , and the number of normal modes excluding rotations and translations n'_i , appearing against each IR are found. The results are shown in table 1.

The character $\chi^t(R)$ of any operation R in the reducible representation defined by the linear combination of the components of a vector (electric moment vector) is found. The normal modes coming under any IR are classified as active or inactive in infrared absorption using the same formula as in paper I, and the results are presented in table 1.

Similarly the character $\chi^R(R)$ of any R in the reducible representation defined by the linear combination of the components of a second rank symmetric tensor (polarizability tensor) is found. The normal modes are classified as active or inactive in

*In these two right handed systems, in this particular example, the coordinate axes $X_{21}, X_{23}; X_{31}, X_{33}$ are superfluous and are not needed for the complete description of the symmetry operations of the molecule. Hence they may be dropped.

Raman scattering using the usual rule and the results are given in table 1. It is found that the number of fundamental normal modes active in Raman scattering is fifteen, which is in good agreement with the number that has been experimentally reported by Becher (1957).

3. Wigner's method and its extension for obtaining the symmetry coordinates:

Wigner's (1930) group theoretical method for obtaining the symmetry coordinates of a rigid molecule is well-known and may be found in detail in Bhagavantham and Venkatarayudu (1969). We present, in what follows, the major steps in extending it to the case of nonrigid molecules—considering the specific example of BF_2CH_3 molecule.

Through the equilibrium position of each atom of the molecule, let a system of axes X_1, X_2, X_3, X_4, X_5 parallel to the one described in § 2 be introduced. Let $x_1^r, x_2^r, x_3^r, x_4^r, x_5^r$ be the coordinates of the r th atom in its displaced position referred to the axes fixed at its equilibrium position. Then any vibrational state of the molecule could completely be defined by the $5n(n=7)$ coordinates. In other words, all the symmetry coordinates may be expressed as linear functions of these $5n$ coordinates.

To obtain the normal coordinates that belong to a nondegenerate IR, Γ_i , one starts with the most general expression Q in the $5n$ coordinates. If R is a symmetry operation and λ its character in Γ_i , one obtains RQ and writes $RQ = \lambda Q$. If the number of normal modes n_i coming under Γ_i is only one, the normal coordinate Q is uniquely determined. On the other hand, if n_i is greater than one, Q involves n_i arbitrary constants and can be expressed in the form (Bhagavantham and Venkatarayudu 1969)

$$Q = a_1 S_1 + a_2 S_2 + \dots + a_{n_i} S_{n_i},$$

where a_1, a_2, \dots, a_{n_i} are arbitrary constants and S_1, S_2, \dots, S_{n_i} are functions of these $5n$ coordinates transforming separately under various R in the same way as Q . In such a case, the actual normal coordinates can be found only when the forces operating on the molecule are known. These functions S_1, S_2, \dots, S_{n_i} are known as symmetry coordinates and the normal coordinates are linear combinations of these symmetry coordinates with suitable coefficients depending upon force constants. One may note that Wigner's method is useful to obtain the symmetry coordinates only.

In order to find the symmetry coordinates belonging to a degenerate IR, Γ_i , of dimensions r , the little group technique (Krishna Murty *et al* 1978) will be useful. They can also be obtained following Bhagavantham and Venkatarayudu (1969):

“Take r most general linear expressions in the $5n$ coordinates Q_1, Q_2, \dots, Q_r and obtain RQ_i and write $RQ_i = \sum a_{ik} Q_k$, where $\{a_{ik}\}$ is the representative matrix of R in the IR Γ_i . Proceed in the same way as in the case of nondegenerate representation.”

The actual determination of the symmetry coordinates of the molecule BF_2CH_3 is carried out in the next section, using the above method and the little group technique (Krishna Murty *et al* 1978).

4. Symmetry coordinates of BF_2CH_3

Following the extension of Wigner's method outlined in § 3, we determine the symmetry coordinates of BF_2CH_3 . We start with a general linear expression

$$Q = \sum_{i=1}^5 a_i x_i^1 + b_i x_i^2 + c_i x_i^3 + d_i x_i^4 + e_i x_i^5 + f_i x_i^6 + g_i x_i^7,$$

where x_i^j stands for the j th component of the i th atom in its displaced position and a_i, b_i, \dots are arbitrary constants. Using the method sketched in § 3 we obtain the symmetry coordinates appearing against various one-dimensional representations as:

$$\begin{aligned} A'_1 : Q &= a_2(x_2^1 + x_2^2) + b_2(x_2^2 + x_2^3) + d_2x_2^4 + e_2x_2^5 + f_2(x_2^6 + x_2^7) \\ &+ a_4(x_4^1 + x_4^2) + b_4(x_4^2 + x_4^3) + c_4(x_4^3 + x_4^5) + d_4(x_4^4 + x_4^5) \\ &+ e_4(x_4^5 + x_4^6) + f_4(x_4^6 + x_4^7 + x_5^6 + x_5^7), \end{aligned}$$

$$A'_2 : Q = f_2(x_2^6 - x_2^7) + f_4[(x_4^6 - x_4^7) + (x_5^6 - x_5^7)],$$

$$\begin{aligned} A''_1 : Q &= b_2(x_2^2 - x_2^3) + a_4(x_4^1 - x_4^2) + b_4(x_4^2 - x_4^3) + c_4(x_4^3 - x_4^5) \\ &+ d_4(x_4^4 - x_4^5) + e_4(x_4^5 - x_4^6) + f_4[(x_4^6 + x_4^7) - (x_5^6 + x_5^7)], \end{aligned}$$

$$A''_2 : Q = f_4[(x_4^6 - x_4^7) - (x_5^6 - x_5^7)].$$

The symmetry coordinates appearing against degenerate IRs are found using the little group technique. Clearly, C_3 is the normal subgroup of $C_3 \otimes C_{2v}$. Its character table is

	E	c_3^+	c_3^-
Γ_1	1	1	1
Γ_2	1	w	w^2
Γ_3	1	w^2	w

The IR Γ_1 forms a star by itself, while Γ_2 and Γ_3 form another star. The little group $L_2(C_3 \otimes C_{2v}, C_3, \Gamma_2)$ of Γ_2 is the cyclic group with $c_2c_3^+$ ($= P$ say) as generator, its kernel K_2 being W . The character table of L_2/K_2 is:

$L_2/K_2 \equiv L_2$	E	P^5	P^4	P^3	P^2	P
R_1	1	1	1	1	1	1
R_2	1	$-w^*$	w	-1	w^*	$-w^*$
R_3	1	w	w^*	1	w	w^*
R_4	1	-1	1	-1	1	-1
R_5	1	w^*	w	1	w^*	w
R_6	1	$-w$	w^*	-1	w	$-w^*$

It may easily be seen that the IRs R_2 and R_3 are the two allowable irreducible representations. R_2 induces E'' , while R_3 induces E' of the group $G=C_3 \otimes C_{2v}$.

Following Krishna Murty *et al* (1978), the symmetry coordinates appearing against the IRs E' and E'' are found:

$$E' : Q = b_1 [(x_1^2 - x_1^3) + i(x_3^2 - x_3^3)]$$

$$E'' : Q = a_1 (x_1^1 - ix_3^1) + b_1 [(x_1^2 + x_1^3) - i(x_3^2 + x_3^3)]$$

$$+ d_1 (x_1^4 - ix_3^4) + e_1 (x_1^5 - ix_3^5) + f_1 (x_1^6 - ix_3^6) + g_1 (x_1^7 - ix_3^7).$$

5. Discussion

Following Crawford and Wilson (1941), Fleming and Banwell (1969) obtained the symmetry coordinates of the molecule BF_2CH_3 in terms of internal coordinates. Since the period of internal rotation will be much greater than that of a vibration, they considered the internal angle τ to be effectively fixed during the course of one vibration. Thus, they obtained the symmetry coordinates that depend parametrically on τ . They obtained fourteen symmetry coordinates for this molecule. This number satisfies the formula, given by Crawford and Wilson (1941), that the number of normal coordinates that do not depend upon M internal coordinates (in this example $M = 1$, the τ alone) is $3n-6-M$ (here, $n=7$, $M=1$).

It may be observed that, using the present method, symmetry coordinates that do not depend upon the internal angle τ can be recovered by ignoring the fourth and fifth coordinates of each atom in the expressions for the symmetry coordinates. Thus we get,

$$S_1 = x_2^1; \quad S_2 = x_2^2 + x_2^3; \quad S_3 = x_2^4; \quad S_4 = x_2^5;$$

$$S_5 = x_2^6 + x_2^7; \quad S_6 = x_2^6 - x_2^7; \quad S_7 = x_2^2 - x_2^3;$$

$$S_8 = (x_1^2 - x_1^3) + i(x_3^2 - x_3^3); \quad S_9 = x_1^1 - ix_3^1;$$

$$S_{10} = (x_1^2 + x_1^3) - i(x_3^2 + x_3^3); \quad S_{11} = x_1^4 - ix_3^4;$$

$$S_{12} = x_1^5 - ix_3^5; \quad S_{13} = x_1^6 - ix_3^6; \quad S_{14} = x_1^7 - ix_3^7.$$

These fourteen symmetry coordinates are obtained for fixed internal orientation of the molecule (since fourth and fifth coordinates are ignored) and may be corresponded with the fourteen coordinates given by Fleming and Banwell (1969).

To summarise the contents of this paper—the extension of Wigner's group theoretical method presented in paper I, has again been applied to the example of BF_2CH_3 and the results obtained agree well with those experimentally reported by Becher (1957). Group theoretical method of obtaining the symmetry coordinates of a molecule has been shown to be, in general, extendable to nonrigid molecules with free internal rotations also, by considering the example of BF_2CH_3 . The method can as well be applied straightaway to such molecules. The number of symmetry coordinates obtained in particular for fixed internal orientation of the molecule BF_2CH_3 agrees with that reported by earlier workers.

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