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In the Classroom

Group Theory Calculations Involving Linear Molecules

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In this paper we show how linear molecules such as CO_2, C_2H_2, and HCN can be treated using the point groups C_{nv} or D_{nh} for general values of n.

Most chemistry courses involving group theory do not treat the infinite point groups $C_{\infty v}$ or $D_{\infty h}$. Even the character tables themselves are not transparent looking, with the profusion of ellipses. Because of this, it is not possible to deduce the vibrational symmetry modes of CO_2, even though the symmetric, asymmetric stretch, and doubly-degenerate bending modes are discussed in almost all physical chemistry courses. In this paper we show how linear molecules such as CO_2, C_2H_2, and HCN can be treated using the point groups C_{nv} or D_{nh} for general values of n. When determining which irreducible representations comprise the normal vibrational modes of a linear molecule such as CO_2, we show that the n-dependence vanishes. The calculations presented here do not require advanced mathematical knowledge and could be incorporated into an undergraduate chemistry curriculum in which group theory is presented.

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Introduction

One of the nicest applications of group theory is the elucidation of the vibrational symmetry modes of molecules. To do this, we determine the (reducible) representation Γ_{3N} based on the cartesian coordinates assigned to each of the N atoms in the molecule, and then use the equation [1]

$$a_{i\Gamma} = \frac{1}{h} \sum_{\hat{R}} n_i(\hat{R}) \chi_i(\hat{R}) \chi_\Gamma(\hat{R}) \tag{1}$$

to decompose Γ_{3N} into the irreducible representations of the point group of the molecule. In Equation (1), $a_{i\Gamma}$ is the coefficient for the ith irreducible representation, h is the order of the group, $n_i(\hat{R})$ is the number of symmetry operations in the class containing the symmetry operator $\hat{R}$, χ_i is the character in the *i*th irreducible representation, and $\chi_\Gamma$is the character in the reducible representation. Using these coefficients, the irreducible representations corresponding to rotation (Γ_{rot}) and translation (Γ_{trans}) can be subtracted, leaving the irreducible representations corresponding to the normal vibrational modes (Γ_{vib}) of the molecule. For non-linear molecules which belong to finite point groups, this task is easily done; however, this is not an elementary task for linear molecules that belong to the point groups $C_{\infty v}$ and $D_{\infty h}$.

In the past, several methods of treatment for the infinite point groups have been presented. Strommen and Lippincott [2] used the irreducible representations and symmetry operations corresponding to point groups of lower symmetry to generate the coefficients $a_{i\Gamma}$. Specifically, they used the groups C_{2v} and D_{2h}. While the correct irreducible representations for Γ_{vib} were obtained, their method does not appear to be rigorous. Jaffé and David [3] used the theory of continuous groups to generate the character tables for the infinite point groups; however, the knowledge of advanced group theory makes this approach impractical for use in undergraduate chemistry courses. Huang and Wang [4] used Equation (1) explicitly for treatment of the infinite point groups and obtained the correct form of Γ_{vib} in each case. This method involves infinite series and a rather complex and confusing method of showing that each series either vanishes or is equal to some multiple of h. Additionally, the character tables used for this study were never mentioned, despite the fact that character tables for infinite point groups have different symmetry operators in different textbooks [1], [5], [6]. Again, the nonrigorous nature of the approach also makes it impractical for the classroom. A new approach presented by Lie [7] uses the general character tables C_{nv} or D_{nh} to determine the irreducible representations that correspond

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to normal vibrational modes in linear molecules; however, the character tables presented for the groups C_{nv} or D_{nh} differ according to the parity of n. Lie's method never took this into account, and the limit $n \to \infty$ appears to have been taken.

What is presented here is a new method for treating the infinite point groups that involves a basic knowledge of group theory, elementary algebra, and trigonometry for a centrosymmetric molecule.

Method

For the linear XYZ molecule (e.g., HCN) of $C_{\infty v}$ symmetry, we use the character table given in Table 1 for C_{nv}, n odd. The character tables for the groups C_{nv} (n odd or n even) can be generated by examining the character tables for the groups C_{3v}, C_{4v}, C_{5v}, and C_{6v} [6]. For C_{nv}, n odd, the reducible representation is

C_{nv}, n odd	E	C_n^j	σ_v
Γ_{3N}	9	$3\left[1 + 2\cos\left(\frac{2\pi j}{n}\right)\right]$	3

Here $j = 1, 2, \ldots, (n-1)/2$. The number of classes C_n^j depends on the value of n. For C_{3v} there is only one such class, C_3. For C_{5v} there are two classes, C_5^1 and C_5^2. For the general case C_{nv} there will be $(n-1)/2$ classes of this type. The order of the group is then given by

$$\begin{aligned} h &= 1 + 2\left[\frac{(n-1)}{2}\right] + n \\ h &= 2n \end{aligned} \quad (2)$$

Information such as the group order and the number of classes, which is needed to determine the $a_{i\Gamma}$ can be found at the bottom of each character table. The characters in Γ_{3N} are obtained by noting the transformation properties of the three cartesian coordinates located on each atom, or by using the methods of Levine [1, pp. 437–438]. Equation (1) gives the number of times that each irreducible representation appears in the reducible

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TABLE 1. Character Table for C_{nv}, n odd

	E	$2C_n^j$	$n\sigma_v$	
A_1	1	1	1	z
A_2	1	1	-1	R_z
E_1	2	$2\cos\left(\frac{2\pi j}{n}\right)$	0	$(x, y); (R_x, R_y)$
E_N	2	$2\cos\left(\frac{2\pi Nj)}{n}\right)$	0	

Order $= 2n$ — $j = 1, 2, \ldots, \frac{n-1}{2}$

Classes $= (n+3)/2$ — $N = 2, \ldots, \frac{n-1}{2}$

representation:

$$a_{A_1} = \frac{1}{2n}\left\{1\cdot 1\cdot 9 + 2\cdot 1\cdot 3\sum_{j=1}^{(n-1)/2}\left[1 + 2\cos\left(\frac{2\pi j}{n}\right)\right] + n\cdot 1\cdot 3\right\}$$
$$= \frac{1}{2n}[9 + 3(n-1) - 6 + 3n]$$
$$= 3$$

The terms in curly brackets above follow the prescription given in Equation (1). For example the term $1\cdot 1\cdot 9$ corresponds to the operation E. The numbers 1, 1, and 9 correspond to the number of symmetry operations in the class E, the character for E in the irreducible representation, and the character of E in the reducible representation. The necessary summations are given in Table 2 [8]. Similarly,

$$a_{A_2} = \frac{1}{2n}\left\{1\cdot 1\cdot 9 + 2\cdot 1\cdot 3\sum_{j=1}^{(n-1)/2}\left[1 + 2\cos\left(\frac{2\pi j}{n}\right)\right] + n\cdot(-1)\cdot 3\right\}$$
$$= \frac{1}{2n}[9 + 3(n-1) - 6 - 3n]$$
$$= 0$$

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TABLE 2. Series Used in the Calculations

n odd	n even
$\sum_{j=1}^{\frac{n-1}{2}} \cos\left(\frac{2\pi j}{n}\right) = -\frac{1}{2}$	$\sum_{j=1}^{\frac{n-2}{2}} \cos\left(\frac{2\pi j}{n}\right) = 0$
$\sum_{j=1}^{\frac{n-1}{2}} \cos\left(\frac{2\pi Nj}{n}\right) = -\frac{1}{2}$	$\sum_{j=1}^{\frac{n-2}{2}} (-1)^j = \left\{\begin{array}{ll} -1, & \frac{n}{2} \text{ even} \\ 0, & \frac{n}{2} \text{ odd} \end{array}\right\}$
$\sum_{j=1}^{\frac{n-1}{2}} \cos\left(\frac{2\pi Nj}{n}\right)\cos\left(\frac{2\pi j}{n}\right) = \left\{\begin{array}{l} \frac{n-2}{4}, N=1 \\ -\frac{1}{2}, N>1 \end{array}\right\}$	$\sum_{j=1}^{\frac{n-2}{2}} (-1)^j \cos\left(\frac{2\pi j}{n}\right) = \left\{\begin{array}{ll} 0, & \frac{n}{2} \text{ even} \\ -1, & \frac{n}{2} \text{ odd} \end{array}\right\}$
	$\sum_{j=1}^{\frac{n-2}{2}} \cos\left(\frac{2\pi j}{n}\right) = \frac{n}{4} - 1$
	$\sum_{j=1}^{\frac{n-2}{2}} \cos\left(\frac{2\pi Nj}{n}\right) = \left\{\begin{array}{ll} -1, & N \text{ even} \\ 0, & N \text{ odd} \end{array}\right\}$
	$\sum_{j=1}^{\frac{n-2}{2}} \cos\left(\frac{2\pi Nj}{n}\right)\cos\left(\frac{2\pi j}{n}\right) = \left\{\begin{array}{ll} 0, & N \text{ even} \\ -1, & N \text{ odd} \end{array}\right\}$
	$N > 1$

$$\begin{aligned} a_{E_1} &= \frac{1}{2n}\left\{1\cdot 2\cdot 9 + 2\cdot 2\cdot 3 \sum_{j=1}^{(n-1)/2} \cos\left(\frac{2\pi j}{n}\right)\left[1 + 2\cos\left(\frac{2\pi j}{n}\right)\right] + 0\right\} \\ &= \frac{1}{2n}\left[18 + 12\left(-\frac{1}{2}\right) + 24\left(\frac{n-2}{4}\right)\right] \\ &= 3 \end{aligned}$$

$$\begin{aligned} a_{E_N} &= \frac{1}{2n}\left\{1\cdot 2\cdot 9 + 2\cdot 2\cdot 3 \sum_{j=1}^{(n-1)/2} \cos\left(\frac{2\pi Nj}{n}\right)\left[1 + 2\cos\left(\frac{2\pi j}{n}\right)\right] + 0\right\} \\ &= \frac{1}{2n}\left[18 + 12\left(-\frac{1}{2}\right) + 24\left(-\frac{1}{2}\right)\right] \\ &= 0, \qquad N > 1 \end{aligned}$$

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where, once again, the necessary summations are given in Table 2. Therefore,

$$\Gamma_{3N} = 3A_1 + 3E_1 \qquad [9\,\text{species}]$$

Table 1 shows that

$$\Gamma_{trans} = A_1 + E_1 \qquad [3]$$
$$\Gamma_{rot} = E_1 \qquad [2]$$

and so we have that

$$\Gamma_{vib} = 2A_1 + E_1 \qquad [4]$$

The numbers in brackets refer to the total dimension of each representation. This is analogous to the degrees of freedom associated with each property. The irreducible representations labeled E or Π are two-dimensional, so they each supply two degrees of freedom. Note that this result was obtained without taking the limit $n \to \infty$. Another notation used to describe irreducible representations for the infinite point groups is given in References 1 and 6. For example, using the irreducible representations for $C_{\infty v}$, $\Gamma_{vib} = 2\sum^{+} + \Pi$.

The character table for C_{nv}, n even (Table 3) is quite different than that of C_{nv}, n odd. In this case, Γ_{3N} is

C_{nv}, n even	E	C_n^j	C_2	σ_v	σ_d
Γ_{3N}	9	$3\left[1 + 2\cos\left(\frac{2\pi j}{n}\right)\right]$	-3	3	3

where $j = 1, 2, \ldots, (n-2)/2$. Following the same procedure as the n odd case we see that

$$\Gamma_{3N} = 3A_1 + 3E_1 \qquad [9\,\text{species}]$$

Table 2 shows that

$$\Gamma_{trans} = A_1 + E_1 \qquad [3]$$
$$\Gamma_{rot} = E_1 \qquad [2]$$

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TABLE 3. Character Table for C_{nv}, n even

	E	$2C_n^j$	C_2	$n/2\sigma_v$	$n/2\sigma_d$	
A_1	1	1	1	1	1	z
A_2	1	1	1	-1	-1	R_z
B_1	1	$(-1)^j$	$(-1)^{\frac{n}{2}}$	1	-1	
B_2	1	$(-1)^j$	$(-1)^{\frac{n}{2}}$	-1	1	
E_1	2	$2\cos\left(\frac{2\pi j}{n}\right)$	-2	0	0	
E_N	2	$2\cos\left(\frac{2\pi Nj}{n}\right)$	$2(-1)^N$	0	0	$(x, y)(R_x, R_y)$

Order $= 2\boldsymbol{n}$ $\quad j = 1, 2, \ldots, \frac{n-2}{4}$

#Classes $= (n+3)/2$ $\quad N = 2, \ldots, \frac{n-2}{2}$

and, exactly like the n odd case, we have that

$$\Gamma_{vib} = 2A_1 + E_1 \qquad [4]$$

Now, consider the linear XYX molecule (e.g., CO_2), which has $D_{\infty h}$ symmetry. See Table 4 for the character table corresponding to D_{nh}, n odd. This character table, along with the one for D_{nh}, n even, was generated using direct products [5]. For n odd the point group D_{nh} is the direct product of D_n and σ_h. The first set of operators is simply the D_n operators, while the second set is a product of the D_n operators with σ_h. The operations $\sigma_h \cdot C_n^j$ are improper rotations. The reducible representation Γ_{3N} is

D_{nh}, n odd	E	C_n^j	C_2	σ_v	$\sigma_h \cdot C_n^j$	σ_v
Γ_{3N}	9	$3\left[1 + 2\cos\left(\frac{2\pi j}{n}\right)\right]$	-1	1	$-1 + 2\cos\left(\frac{2\pi j}{n}\right)$	3

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TABLE 4. Character Table for D_{nh}, n odd

	E	$2C_n^j$	nC_2	σ_h	$2\sigma_h \cdot C_n^j$	$n\sigma_v$	
A_1'	1	1	1	1	1	1	
A_2'	1	1	-1	1	1	-1	R_z
E_1'	2	$2\cos\left(\frac{2\pi j}{n}\right)$	0	2	$2\cos\left(\frac{2\pi j}{n}\right)$	0	(x, y)
E_N'	2	$2\cos\left(\frac{2\pi Nj}{n}\right)$	0	2	$2\cos\left(\frac{2\pi Nj}{n}\right)$	0	
A_1''	1	1	1	-1	-1	-1	
A_2''	1	1	-1	-1	-1	1	z
E_1''	2	$2\cos\left(\frac{2\pi j}{n}\right)$	0	-2	$-2\cos\left(\frac{2\pi j}{n}\right)$	0	(R_x, R_y)
E_N''	2	$2\cos\left(\frac{2\pi Nj}{n}\right)$	0	-2	$-2\cos\left(\frac{2\pi Nj}{n}\right)$	0	

Order = n + 6 $\quad N = 2, \ldots, \frac{n-1}{2}$

 # Classes = n + 6 $\quad N = 2, \ldots, \frac{n-1}{2}$

where $j = 1, 2, \ldots, (n-1)/2$. Using Equation (1) and Table 2, we obtain

$$\begin{aligned}
\Gamma_{3N} &= A_1' + 2E_1' + 2A_2'' + E_1'' && [9\,\text{species}]\\
\Gamma_{trans} &= A_2'' + E_1' && [3]\\
\Gamma_{rot} &= E_1'' && [2]\\
\Gamma_{vib} &= A_1' + A_2'' + E_1' && [4]
\end{aligned}$$

For n even, the D_{nh} point group is the direct product of D_n and i, as shown in Table 5. The direct products $i \cdot C_n^j$ represent improper rotations. Note again that the character table for n even is quite different than that for n odd. In this case, Γ_{3N} is

D_{nh}, n even	E	C_n^j	$C_2(z)$	C_2'	C_2''	i	$i \cdot C_n^j$	σ_h	σ_v	σ_d
Γ_{3N}	9	$3\left[1 + 2\cos\left(\frac{2\pi j}{n}\right)\right]$	-3	-1	-3	$-1 - 2\cos\left(\frac{2\pi j}{n}\right)$	1	3	3	

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TABLE 5. Character Table for D_{nh}, n even

	E	$2C_n^j$	$C_2(z)$	$\frac{n}{2}C_2'(x)$	$\frac{n}{2}C_2''(y)$	i	$2i \cdot C_n^j$	σ_h	$n/2\sigma_v$	$n/2\sigma_d$	
A_{1g}	1	1	1	1	1	1	1	1	1	1	
A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1	R_z
B_{1g}	1	$(-1)^j$	$(-1)^{n/2}$	1	−1	1	$(-1)^j$	$(-1)^{n/2}$	1	−1	
B_{2g}	1	$(-1)^j$	$(-1)^{n/2}$	−1	1	1	$(-1)^j$	$(-1)^{n/2}$	−1	1	
E_{1g}	2	$2\cos\left(\frac{2\pi j}{n}\right)$	−2	0	0	2	$2\cos\left(\frac{2\pi j}{n}\right)$	−2	0	0	(R_x, R_y)
E_{Ng}	2	$2\cos\left(\frac{2\pi Nj}{n}\right)$	$2(-1)^N$	0	0	2	$2\cos\left(\frac{2\pi Nj}{n}\right)$	$2(-1)^N$	0	0	
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1	
A_{2u}	1	1	1	−1	−1	−1	−1	−1	1	1	z
B_{1u}	1	$(-1)^j$	$(-1)^{n/2}$	1	−1	−1	$-(-1)^j$	$-(-1)^{n/2}$	−1	1	
B_{2u}	1	$(-1)^j$	$(-1)^{n/2}$	−1	1	−1	$-(-1)^j$	$-(-1)^{n/2}$	1	−1	
E_{1u}	2	$2\cos\left(\frac{2\pi j}{n}\right)$	−2	0	0	−2	$-2\cos\left(\frac{2\pi j}{n}\right)$	2	0	0	(x, y)
E_{Nu}	2	$2\cos\left(\frac{2\pi Nj}{n}\right)$	$2(-1)^N$	0	0	−2	$-2\cos\left(\frac{2\pi Nj}{n}\right)$	$-2(-1)^N$	0	0	

Order $= 4n$ $\qquad j = 1, 2, \ldots, \frac{n-2}{2}$

 # Classes $= \mathbf{n + 6}$ $\qquad N = 2, \ldots, \frac{n-2}{2}$

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where $j = 1, 2, \ldots, (n-2)/2$. Using Equation (1) and Table 2, we find that

$$\begin{aligned}
\Gamma_{3N} &= A_{1g} + E_{1g} + 2A_{2u} + 2E_{1u} && [9\,\text{species}] \\
\Gamma_{trans} &= A_{2u} + E_{1u} && [3] \\
\Gamma_{rot} &= E_{1g} && [2] \\
\Gamma_{vib} &= A_{1g} + A_{2u} + E_{1u} && [4]
\end{aligned}$$

which is exactly the same as the n odd case. As Table 2 indicates, some of the summations required to determine Γ_{3N} depend on the parity of $n/2$ or N; however, these cases always result in the $a_{i\Gamma}$ equal to zero.

Now consider the linear XYYX molecule (e.g., C_2H_2) with $D_{\infty h}$ symmetry. For n odd, we obtain

n odd	E	C_n^j	C_2	σ_h	$\sigma_h \cdot C_n^j$	σ_v
Γ_{3N}	12	$4\left[1 + 2\cos\left(\frac{2\pi j}{n}\right)\right]$	0	0	0	4

where $j = 1, 2, \ldots, (n-1)/2$ and

$$\begin{aligned}
\Gamma_{3N} &= 2A_1' + 2E_1' + 2A_2'' + E_1'' && [12\,\text{species}] \\
\Gamma_{trans} &= A_2'' + E_1' && [3] \\
\Gamma_{rot} &= E_1'' && [2] \\
\Gamma_{vib} &= 2A_1' + A_2'' + E_1' && [7]
\end{aligned}$$

For n even, we find that

n even	E	C_n^j	$C_2(z)$	C_2'	C_2''	i	$i \cdot C_n^j$	σ_h	σ_v	σ_d
Γ_{3N}	12	$4\left[1 + 2\cos\left(\frac{2\pi j}{n}\right)\right]$	-4	0	0	0	0	0	4	4

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where $j = 1, 2, \ldots, (n-2)/2$, and

$$\begin{aligned}
\Gamma_{3N} &= 2A_{1g} + 2E_{1g} + 2A_{2u} + 2E_{1u} && \text{[12 species]}\\
\Gamma_{trans} &= A_{2u} + E_{1u} && [3]\\
\Gamma_{rot} &= E_{1g} && [2]\\
\Gamma_{vib} &= 2A_{1g} + A_{2u} + E_{1g} + E_{1u} && [7]
\end{aligned}$$

Note that once again we have the same result with n even as with n odd.

Conclusion

The method used in the above examples treats the cases of C_{nv} and D_{nh}, where n is arbitrary. When applying Equation 1 to linear molecules, the n-dependence on the coefficients $a_{i\Gamma}$ vanishes, so that the limit $n \to \infty$ never becomes necessary. This is a straightforward method that follows the standard group theory approach for determining the normal vibrational modes in molecules and could be included as a group or individual project in any undergraduate class in which group theory is introduced. Recently, spreadsheets have been used for similar calculations involving other point groups [9]. Spreadsheet calculations could be performed for the infinite point groups using the procedure outlined here.

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