Group Theory Applications: Infra-red Spectral Assignment

Nilar Kyi and **David T. Win***
Department of Chemistry, Yangon University
Yangon, Myanmar

Abstract

Group theory principles were applied and the transformation of the x, y, z vectors on each atom caused by symmetry operations were observed to obtain the 3N basis vector representations é3N, of $NiCl_4$, Al_2Cl_6 *and* $Fe(CO)_5$*. The identified infra-red active modes and Raman active modes were then assigned to the experimental spectral frequencies by using the projection operator method.*

***Keywords**: Vibrational mode, vibrational spectrum, infra-red, Raman spectrum, symmetry, group theory, projection operator, spectral frequency assignment.*

Introduction

The number, types and the selection rules for vibrational transitions may be determined solely by reference to symmetry properties of molecules (Thomas 1974). Such symmetry simplifies the analysis of vibrational modes and vibrational spectra (Alberty and Daniels 1979). Molecular symmetry allows prediction of its infra-red or Raman spectrum; and *vice versa* (Ferraro and Ziomek 1975). The vibrational modes of a molecule may be classified into various types, such as bond stretches, and bond angle deformations. It is possible to determine the number and symmetry species of each type.

Continued interest in the field is shown by the appearance of many publications such as Buchachenko and Stepanov (1996); Eryomin *et al.* (1996 & 2000); and Scherbinin *et al.* (1996).

Group theory by itself cannot predict the frequency of a particular vibration, but fairly accurate guesses can be made when combined with accumulated experiences of molecular spectroscopists (Cotton 1971; Kyi 1990).

The prediction requires a number of molecular structural parameters, such as bond lengths and bond angles, in addition to a knowledge of appropriate force constants. Then Wilson's F and G matrix method is applied after constructing the required symmetry adapted linear combinations (SALC). (Wilson *et al.* 1955).

In principle the vibrational spectrum of any molecule can be analyzed to give specific frequency assignment to every vibrational mode. But in practice, several complicating factors must be taken into account. Factors such as combination bands, difference bands and overtone bands caused by combination of fundamental vibrations; ambiguities with respect to molecular or ionic structure (Davidson 1971); accidental degeneracy; and Fermi resonance (Siebrt 1966).

Vibrational Mode Assignment of Some Molecules and Ions

Nickel Tetrachloride Ion

For vibrational mode classification, the normal modes are expressed as functions of a set of internal displacement vectors which yield information on bond stretching and bond bending contributions to different symmetry normal modes (Cotton 1971). The projection operator method is a very powerful method for explicit information on vector bases for irreducible representations (Wilson *et al.* 1955).

The ion has a square planar structure with a nickel ion at the center of a square plane, surrounded by four chloride ions at the corners. Hence it has a D_{4h} symmetry (Kyi and Win 2001). The four Ni-Cl bonds which lie in a square planar structure of the nickel tetrachloride ion can stretch and contract in various combi-nations and are designated as bond stretching internal displacement vectors v_1, v_2, v_3 and v_4.

The same four Ni-Cl bonds can move above and below the plane of the ion structure, giving rise to four out-of-plane deformation vectors d_1, d_2, d_3, and d_4, another set of internal displacement vectors.

The four Cl-Ni-Cl bond angles can expand and contract, giving yet another set of internal displacement vectors δ_1, δ_2 , δ_3, and δ_4 called in-plane deformation vectors.

The Γstr. is found by using the above bond stretching internal displacement vectors v_1, v_2, v_3 and v_4 as basis. By applying the same procedure as before (Kyi and Win 2001). The irreducible representation obtained from the D_{4h} point group tables, yield the following result.

Γstr. = $A_{1g} \oplus B_{1g} \oplus E_u$ ....(1)

Similarly Γopd is found by using the above four out-of-plane deformation internal displacement vectors d_1, d_2 , d_3, and d_4 as basis.

Γopd = $E_g \oplus A_{2u} \oplus B_{2u}$ ....(2)

Γ3N (genuine vibrations) does not contain E_g (Win and Kyi 2000), hence it must correspond to a pair of redundant coordinates. E_g is thus neglected.

Γopd = $A_{2u} \oplus B_{2u}$ ....(3)

Γipd is obtained by using the δ_1, δ_2 , δ_3, and δ_4 as basis.

Γipd = $A_{1g} \oplus B_{1g} \oplus E_u$ ....(4)

The A_{1g} is redundant as all four angles increasing or decreasing simultaneously in a plane is physically impossible. Hence it is neglected. Thus:

Γipd = $B_{1g} \oplus E_u$ ....(5)

In some cases, such as NiCl bond stretches, fundamental modes may be found by applying projection operators P.

Stretching Modes

The operation of the projection operators of A_{1g}, B_{1g} and E_u symmetries (Equation 1) on v_1 yield the following:

$$P[A_{1g}]v_1 = v_1 + v_2 + v_4 + v_3 + v_1 + v_3 + v_2 + v_4 + v_3 + v_2 + v_4 + v_1$$
$$= 4v_1 + 4v_2 + 4v_3 + 4v_4$$
$$= v_1 + v_2 + v_3 + v_4 \quad \text{.............(6)}$$

$$P[B_{1g}]v_1 = v_1 - v_2 + v_3 - v_4 \quad \text{..............(7)}$$

$$P\,[E_u]v_1 = v_1 - v_3 \quad \text{..............(8)}$$

Equation 6 shows that the A_{1g} mode includes simultaneous equal amplitude bond stretching of all four bonds.

Equation 7 shows that the B_{1g} modes has one pair of bonds (v_1 & v_3) are out of phase by π from another pair of bonds (v_2 & v_4) i.e. while one pair is stretching the other pair is contracting.

Equation 8 shows that in the E_u mode the pair of bonds (v_2 & v_4) do not vibrate while (v_1 & v_3) are in opposite phase. Since the E_u mode is doubly degenerate it will contain two fundamental modes. The reduction of E_u will yield two representations involving complex numbers e and e* (complex conjugate), from which the two true fundamental modes can be determined.

Out-of-plane Deformation

$$P[A_{2u}]\ d_1 = d_1 + d_2 + d_3 + d_4 \text{ .... } (9)$$

$$P[B_{2u}]\ d_1 = d_1 - d_2 + d_3 - d_4 \text{ .... } (10)$$

Equation 9 shows that all four bonds simultaneously bend upwards from the plane, in-phase and to the same extent. Equation 10 shows bonds 1 and 2 bend upwards while 2 and 4 bend downwards to the same extent.

In-plane Deformation

$$P[A_{2u}]\ \delta_1 = \delta_1 + \delta_2 + \delta_3 + \delta_4 \text{ ....} (11)$$

$$P[B_{2g}]\ \delta_1 = \delta_1 - \delta_2 + \delta_3 - \delta_4 \text{...........} (12)$$

$$P\ [E_u]\ \delta_1 = \delta_1 - \delta_3 \text{ ………….............} (13)$$

Equation 11 shows the simultaneous expansion of all four angles. It is physically impossible and is therefore redundant. Equation 12 shows that the pair of angles (δ_1 & δ_3) expand while the other pair of angles (δ_2 & δ_4) contract, i.e. elongation of a pair of two opposing sides of the square planar ion structure at the same time when the other pair of two opposing sides is contracting. Equation 13 shows that angle δ_1 expands while angle δ_3 contracts and vice versa. In other words when angle δ_1 expands the side extending that angle expands while the side extending angle δ_3 contracts; and when angle δ_1 contracts the side extending that angle contracts while the side extending angle 3 expands.

Aluminum Chloride

The molecule has a square planar shape with two chlorine - Cl and two aluminum - Al atoms at alternate corners. Each of the two aluminum atoms have two other chlorine atoms attached, forming $AlCl_2$ groups which extend outside the base square plane. Thus the molecule has a D_{2h} symmetry (Win and Kyi 2001).

The four sides of the square planar base are designated as bond stretching internal displacement vectors v_1, v_2, v_3 and v_4. The four Al-Cl bonds extending outside the square planar base are labeled v_5, v_6, v_7 and v_8. These describe the stretching modes.

The angles surrounding one Al atom, on one corner of the square planar base, are denoted as δ_1, δ_2, δ_3, and δ_4, starting from the inner angle going in a clockwise direction. Similar angles δ_5, δ_6, δ_7, and δ_8 are defined for the angles surrounding the other Al atom. The two angles Al-Cl-Al on opposite corners of the square planar base are δ_9 and δ_{10}. These constitute the in-plane internal displacement vectors.

The eight bonds, four on each Al atom, can move up and down from the base plane. These angles are denoted d_1, d_2, d_3, d_4, d_5, d_6, d_7, and d_8 . The projection operators are applied as before and the results obtained are shown in Table 1.

Iron Carbonyl

The molecule has a triangular base with Fe at the center and three carbon atoms at the three apexes. Each of the carbon atoms is bonded to an oxygen atom forming a carbonyl group >C=O. Thus, there are three carbonyl groups at the apexes. In addition there are two carbonyl groups outside the base plane, one above and one below the base plane. It belongs to the D_{3h} point group (Cotton *et al.* 1958; Ware 1970).

The Fe-C bonds in the base plane are designated as v_1, v_2, and v_3. The associated carbonyl bonds are designated as v_4, v_5, and v_6. The Fe-C bonds above and below the base plane are designated as v_7 and v_8; and the associated carbonyl bonds are designated as v_9 and v_{10}.

The three angles surrounding the Fe atom in the base plane are named δ_1, δ_2, and δ_3. The angles on each side of the three carbon atoms in the apex carbonyl groups are called δ_4 and δ_5; δ_6 and δ_7; and δ_8 and δ_9. These are the in-plane bending vectors.

The three Fe-C bonds in the base plane d_1, d_2, and d_3 and the three >C=O bond d_4, d_5, and d_6 are out-of-plane bending vectors.

The projection operators are applied as before and the results obtained are shown in table 2. It is interesting to note that application of the projection operator $P[E']$ on δ_4 annihilates δ_5, δ_7, and δ_9 out of a six member set of vectors $\{\delta_4, \delta_6, \delta_8, \delta_5, \delta_7, \delta_9\}$. The same operator $P[E']$ on δ_5 annihilates δ_4, δ_6, and δ_8. This is because the sub-sets $\{\delta_5, \delta_7, \delta_9\}$ and $\{\delta_4, \delta_6, \delta_8\}$ are not independent with respect to C_2 and σ_v. Thus the operator $P[E']$ is applied to both subsets. Hence it is advisable to be on the look out for cases where some elements of a basis set disappear on application of a projection operator.

Frequency Assignment

Group theory can be used up to this stage only. It can only reveal the number and symmetry types of the different possible modes. For assignment of known frequencies theoretical calculations using F and G matrices, based on molecular properties such as group-masses, bond strengths and force constants, are required. The calculations yield frequencies for specific modes. The experimental frequency nearest to the calculated frequency is assigned that mode. Frequency assignment of Al_2Cl_6 modes is shown in Table 3 (Klemperer 1956).

Conclusion

The difficulty of vibrational analysis increases with structural complexity. This is partly because structural complexity makes complete identification of internal coordinates (true basis vectors) difficult. Some coordinates can often be missed out.

Thus it is advisable to check that:

Γvibration (genuine) = $\Sigma_i \Gamma i$, where Γi are Γstr , Γipd , Γopd ... etc...

Acknowledgement

The authors are indebted to Yangon University and Assumption University for permission to accomplish this work.

References

Alberty, R. A.; and Daniels, F. 1979. Physical Chemistry, 5th ed. John Wiley, New York.

Buchachenko, A.A.; and Stepanov, N. F. 1996. Ar-I2 Interactions: Models based on the diatomics in molecule approach. J. Chem. Phys. 104 (24): 9913-25.

Cotton, F.A. 1971. Chemical applications of group theory. John Wiley, New York.

Cotton, F.A.; Danti, A.; Waugh, J.S.; and Fessender, R.W. 1958. Vibrational modes. J. Chem. Phys. 29:1427-40.

Davidson, G. 1971. Introductory group theory for chemists. Applied Science Publ., London.

Eryomin, V.V.; Kuz'menko, N. E.; and Umanskii, I. M. 1996. Interference effects in wave packet dynamics at the pulse optical excitation of a diatomic molecule. Khim.Fiz. 15 (5): 5-12 .

Eryomin, V.V.; Kuz'menko, N.E.; and Umanskii, I.M. 2000. Wavepacket dynamics in the ground electronic state of a diatomic molecule. Chem. Phys. Lett. 316 (3-4): 303-10.

Ferraro, J.R.; and Ziomek, J.S. 1975. Introductory group theory and its application to molecular structure. 2nd ed. Plenum Press, New York.

Klemperer, W. 1956. J. Chem. Phys. 24: 353-7.

Kyi, N. 1990. Group Theory - Applications in Vibrational Analysis. M. Phil. dissertation. Yangon University, Yangon, Myanmar.

Kyi, N.; and Win, D.T. 2001. Group theory applications to vibrational modes. AU J.T. 5: 1-4.

Scherbinin, A.V.; Pupyshev, V.I.; and Stepanov, N.F. 1996. On the use of multipole expansion of the Coulomb potential in quantum chemistry. Int. J. Quant. Chem. 60: 843-52.

Siebrt, H. 1966. Anwendungen der Schwingungsspektroskopie in der Anorganischen Chemie. Springer, Berlin.

Thomas, C.H. 1974. Group theory applications. J. Chem. Ed. 51: 91-7.

Ware, M. J. 1970. Physical methods in advanced inorganic chemistry. Interscience, London.

Wilson, E.B., Jr.; Decius, J.C.; and Cross, P.C. 1955. Molecular Vibrations. McGraw-Hill, New York.

Table 1. Fundamental modes of Al_2Cl_6

Mode	Projector	Projected vector	Remarks
Stretching $2A_g$	$P[A_g]v_1$	$v_1 + v_2 + v_3 + v_4$	in-phase stretch
	$P[A_g]v_5$	$v_5 + v_6 + v_7 + v_8$	
$2B_{1g}$	$P[B_{1g}]v_1$	$v_1 - v_2 + v_3 - v_4$	two opposing sets
	$P[B_{1g}]v_5$	$v_5 - v_6 + v_7 - v_8$	
$2B_{2u}$	$P[B_{2u}]v_1$	$v_1 + v_2 - v_3 - v_4$	redundant mode
	$P[B_{2u}]v_5$	$v_5 + v_6 - v_7 - v_8$	
$2B_{3u}$	$P[B_{3u}]v_1$	$v_1 - v_2 - v_3 + v_4$	
	$P[B_{3u}]v_1$	$v_5 - v_6 - v_7 + v_8$	
In-plane bend $4A_g$	$P[A_g]\,\delta_1$	$\delta_1 + \delta_7$	
	$P[A_g]\,\delta_6$	$\delta_9 + \delta_{10}$	
	$P[A_g]\,\delta_5$	$\delta_3 + \delta_5$	
	$P[A_g]\,\delta_9$	$\delta_2 + \delta_4 + \delta_6 + \delta_8$	
$1B_{1g}$	$P[B_{1g}]\,\delta_1$	0	
	$P[B_{1g}]\,\delta_6$	$\delta_4 + \delta_6 - \delta_2 - \delta_8$	
	$P[B_{1g}]\,\delta_5$ & $P[B_{1g}]\,\delta_9$	0	
$2B_{2u}$	$P[B_{2u}]\,\delta_1$	0	
	$P[B_{2u}]\,\delta_6$	$\delta_2 - \delta_4 + \delta_6 - \delta_8$	
	$P[B_{2u}]\,\delta_5$	0	
	$P[B_{2u}]\,\delta_9$	$\delta_9 - \delta_{10}$	physically impossible
$3B_{3u}$	$P[B_{3u}]\,\delta_1$	$\delta_1 - \delta_7$	physically impossible
	$P[B_{3u}]\,\delta_1$	$\delta_6 + \delta_8 - \delta_2 - \delta_4$	
	$P[B_{3u}]\,\delta_1$	$\delta_5 - \delta_3$	
	$P[B_{3u}]\,\delta_1$	0	
Out-of-plane bend $2B_{2g}$	$P[B_{2g}]\,d_1$	$d_1 + d_2 - d_5$	
	$P[B_{2g}]\,d_3$	$d_3 - d_4 + d_8$	physically impossible
$2B_{3g}$	$P[B_{3g}]\,d_1$	$d_1 - d_2 + d_5$	
	$P[B_{3g}]\,d_3$	$d_3 + d_4 - d_8$	physically impossible
$2A_u$	$P[A_u]\,d_1$	$d_1 - d_2 - d_5$	
	$P[A_u]\,d_3$	$d_3 - d_4 - d_8$	physically impossible
$2B_{1u}$	$P[B_{1u}]\,d_1$	$d_1 + d_2 + d_5$	
	$P[B_{1u}]\,d_3$	$d_3 + d_4 + d_8$	

Table 2. Fundamental modes of Fe $(CO)_5$

Mode	Projector	Projected vector	Remarks
Stretching $4A_1'$	$P[A_1']v_1$	$v_1 + v_2 + v_3$	non-redundant
	$P[A_1']v_8$	$v_8 + v_9$	physically possible
	$P[A_1']v_7$	$v_7 + v_{10}$	modes
	$P[A_1']v_4$	$v_4 + v_5 + v_6$	
$2E'$	$P[E']v_1$	$2v_1 - v_2 - v_3$	non-redundant
	$P[E']v_8$ & $P[E']v_7$	0	possible modes
	$P[E']v_4$	$2v_4 - v_5 - v_6$	
$2A_2''$	$P[A_2'']v_1$	0	non-redundant
	$P[A_2'']v_8$	$v_8 - v_9$	possible modes
	$P[A_2'']v_7$	$v_7 - v_{10}$	
	$P[A_2'']v_4$	0	
In-plane bend $2A_1'$	$P[A_1']\delta_1$	$\delta_1 + \delta_2 + \delta_3$	redundant, impossible
	$P[A_1']\delta_4$	$\delta_4 + \delta_5 + \delta_6 + \delta_7 + \delta_8 + \delta_9$	ditto
$3E'$	$P[E']\delta_1$	$2\delta_1 - \delta_2 - \delta_3$	
	$P[E']\delta_4$	$2\delta_4 - \delta_6 - \delta_8$	
	$P[E']\delta_5$	$2\delta_5 - \delta_7 - \delta_9$	
$1A_2'$	$P[A_2']\delta_1$	0	
	$P[A_2']\delta_6$	$\delta_4 - \delta_5 + \delta_6 - \delta_7 + \delta_8 - \delta_9$	
Out-of-plane $2A_2''$	$P[A_2'']d_1$	$d_1 + d_2 + d_3$	
bend	$P[A_2'']d_4$	$d_4 + d_5 + d_6$	two modes are same
$2E''$	$P[E'']d_1$	$2d_1 - d_2 - d_3$	
	$P[E'']d_4$	$2d_4 - d_5 - d_6$	two modes are same
Top & bottom A_1'	$P[A_1']\delta_1$	$\delta_1 + \delta_2 + \delta_3 + \delta_4 + \delta_5 + \delta_6$	all are physically
>C=O bend E'	$P[E']\delta_1$	$2\delta_1 - \delta_2 - \delta_3 + 2\delta_4 - \delta_5 - \delta_6$	impossible modes

A_2''	$P[A_2'']\,\delta_1$	$\delta_1 + \delta_2 + \delta_3 - \delta_4 - \delta_5 - \delta_6$
E''	$P[E'']\,\delta_1$	$2\delta_1 - \delta_2 - \delta_3 - 2\delta_4 + \delta_5 + \delta_6$

Table 3. Al_2Cl_6 Frequencies

Symmetry of fundamental mode	Experimental frequency / cm^{-1}
A_g	ν_1 = 506
	ν_2 = 340
	ν_3 = 217
	ν_4 = 112
Au	ν_5 = ---
B_{1g}	ν_6 = 438
	ν_7 = 164
B_{1u}	ν_8 = 625
	ν_9 = ---
	ν_{10} = ---
B_{2g}	ν_{11} = 606
	ν_{12} = 164
B_{2u}	ν_{13} = ---
	ν_{14} = ---
B_{3g}	ν_{15} = ---
B_{3u}	ν_{16} = 484
	ν_{17} = ---
	ν_{18} = ---