

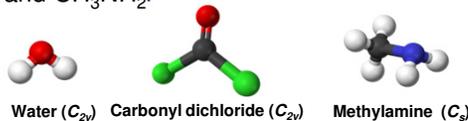
# Prediction and Analysis of IR Spectra using Unified Group Theory

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## Abstract

We studied Standard and Unified group theories. Using a combination of Unified group theory and computer aided analysis, Gaussian09 [1] with GaussView [2] as a GUI and MOLVIB [3], we derived PED (potential energy distribution) data for molecular vibrations. We assigned IR spectra for three molecules: H<sub>2</sub>O, COCl<sub>2</sub> and CH<sub>3</sub>NH<sub>2</sub>.



## The Role of Group Theory

- Information regarding a molecule's symmetry can simplify calculations for molecular vibrational analysis.
- Group theory generates a molecule's internal symmetry coordinates.

## Unified Group Theory: A streamlined approach

- Unified group theory uses fewer, less ambiguous symmetry operations, Table 1.
- Reduction of molecular representations is greatly simplified and streamlined while ultimately providing the same information.

Table 1: Unified group theory notations

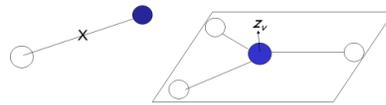
Symmetry operations	Symbol
Do nothing (identity)	<i>E</i>
Rotation by 2π/n radian about x-axis	<i>C<sub>n</sub></i>
Inversion through a center	<i>i</i>
Inversion followed by rotation of 2π/n radian about x-axis	<i>S<sub>n</sub></i>

## The Correspondance Rules & PED

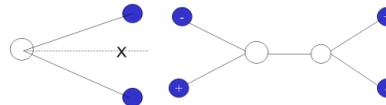
PED results are derived with the use of the Correspondence Rules [4] for internal vibrational coordinates. The transformation properties of four internal coordinates based on these rules are shown in Figure1.

Figure1: Correspondence rules of molecular internal vibration.

(1) Bond stretching    (3) A bond-plane angle change



(2) Valence-angle bending    (4) Bond twisting



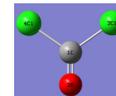
## How is group theory used in determining vibrational frequencies?

- Identify the symmetry elements and the point group.
- Identify the types of internal vibrational coordinates.
- Apply the correspondence rules to find the transformation properties of the internal vibrational coordinates using the Character Table of the point group to reduce the representations to a SALC (symmetry adopted linear combination) of irreducible representations.
- Generate the ISC (internal symmetry coordinates).
- Determine PED of vibrational frequencies.

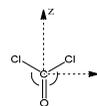
## Carbonyl dichloride

Symmetry elements: *E*, 2<sub>z</sub>, 2<sub>y</sub>, 2<sub>x</sub>; COCl<sub>2</sub> ∈ C<sub>2v</sub>.

Bond stretching	Valence-angle bending	Bond-plane angle change
$s_1 = C_1 - Cl_1$	$\theta_1 = \angle O_1 C_1 Cl_1$	$\lambda_c = \angle O_2 C_1 Cl_1$
$s_2 = C_1 - Cl_4$	$\theta_2 = \angle O_2 C_1 Cl_4$	
$s_3 = C_1 - O_2$		



	C <sub>2v</sub>	E	2 <sub>z</sub>	2 <sub>y</sub>	2 <sub>x</sub>	
A <sub>1</sub>	1	1	1	1	1	1, z, x <sup>2</sup> , y <sup>2</sup> , z <sup>2</sup>
A <sub>2</sub>	1	1	-1	-1	-1	xy, z̄, xyz
B <sub>1</sub>	1	-1	1	-1	-1	zx, ȳ, x
B <sub>2</sub>	1	-1	-1	1	1	yz, x̄, y



As an example apply Correspondence Rule 1 on two equivalent C-Cl bonds: two C-Cl bonds transform like a scalar function.

- Apply the symmetry operations on equivalent scalar *s<sub>1</sub>* and *s<sub>2</sub>*:  

$$\begin{matrix} E & 2_z & 2_y & 2_x \\ 2 & 0 & 0 & 0 \end{matrix} \begin{matrix} s_1 \\ s_2 \end{matrix}$$
- Obtain a linear combination of unirreps which gives the same sum. Therefore the two stretching motions are the sum of two irreducible representations: A<sub>1</sub> + B<sub>2</sub>
- Take the simplest base from each unirrep: From A<sub>1</sub>: 1 and B<sub>2</sub>: *y*.
- The Internal Symmetry Coordinates from SALC's of *s<sub>1</sub>* and *s<sub>2</sub>*:  
 From A<sub>1</sub>: S<sub>1</sub> = *s<sub>1</sub>* + *s<sub>2</sub>*      From B<sub>2</sub>: S<sub>2</sub> = *s<sub>1</sub>* - *s<sub>2</sub>*

Therefore the ISC's of COCl<sub>2</sub>:

$$\text{From } A_1: S_1 = s_1 + s_2 \quad \alpha_1 = \theta_1 + \theta_2 \quad S_{CO} = S_3$$

$$\text{From } B_1: \lambda_c$$

$$\text{From } B_2: S_2 = s_1 - s_2 \quad \alpha_2 = \theta_1 - \theta_2$$

Figure 2 Vibrational modes for COCl<sub>2</sub>.

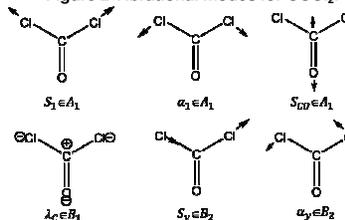
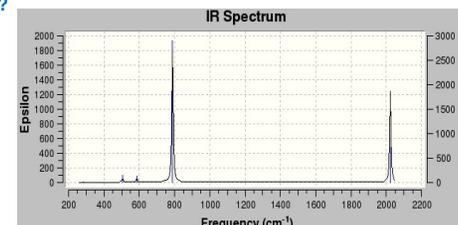


Table 2 Normal mode frequencies for carbonyl dichloride in cm<sup>-1</sup> determined at the HF level of theory using 6-31G\* basis set.

Symmetry	IR Experiment (cm <sup>-1</sup> ) [5]	Our Calculated IR (cm <sup>-1</sup> )	PED from Correspondence Rules	Vibrational frequency Assignments based on PED
A <sub>1</sub>	286	286.6	88.0% s <sub>1</sub> + 11.1% s <sub>2</sub>	CO <sub>2</sub> symmetric deformation
	570	505.5	80.0% s <sub>2</sub> + 10.0% α <sub>1</sub>	C-Cl symmetric stretching
	1827	2023.3	100.0% S <sub>CO</sub>	C-O symmetric stretching
B <sub>1</sub>	580	588.1	100.0% λ <sub>c</sub>	C out of plane lifting
B <sub>2</sub>	440	431.3	66.6% s <sub>2</sub> + 44.4% s <sub>1</sub>	CO <sub>2</sub> asymmetric deformation
	848	788.8	58.8% s <sub>2</sub> + 44.4% α <sub>2</sub>	C-Cl asymmetric stretching

Figure 3: IR spectrum for carbonyl dichloride



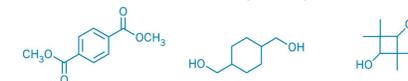
## Conclusion

We successfully assigned IR frequencies of water, carbonyl dichloride and methylamine Normal mode frequencies are determined at the HF level of theory using 6-31G\* basis set. Our results provide insight into the experimentally determined molecular vibrations of these molecules.

## Future Plans

We will calculate IR spectra/PED data for the molecules dimethyl terephthalate, 1,4-cyclohexanedimethanol, and 2,2,4,4-tetramethyl-1,3-cyclobutanediol, which are currently seeing early market application in water bottles as a combined polymer called "Tritan" [6], an alternative to Bisphenol A (BPA) based plastics that don't contaminate stored water.

Figure 4 Dimethyl terephthalate, 1,4-cyclohexanedimethanol, and 2,2,4,4-tetramethyl-1,3-cyclobutanediol,



## Acknowledgements

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