

# Molecular vibrations

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# Molecular vibrations

## Why this is interesting

- ▶ Molecular energy spectra are determined by electronic transitions, molecular vibrations, and molecular rotations
- ▶ Complex molecular vibrations are expressible in terms of simple **normal modes**
- ▶ Generally this type of problem can be solved by solving a system of differential equations, where normal modes will then appear as eigenvectors and have certain, generally different frequencies of oscillation
- ▶ However, these vibrational modes can be characterized by their symmetry properties, each mode “belonging” to an irreducible representation of the system
- ▶ Important spectral properties can be derived without the need to solve differential equations

# Vibrations, rotations and translations

## Example system: $\text{NH}_3$

- ▶ Each atom has three positional degrees of freedom, for a total of 12 in the case of  $\text{NH}_3$
- ▶ Uniform displacement of all atoms in  $x$ ,  $y$  or  $z$  direction would be a translation. Thus three degrees of freedom are translational
- ▶ Similarly, three degrees of freedom are rotational
- ▶ Generally, the remaining  $3n - 6$  degrees of freedom are vibrational
- ▶ In the case of  $\text{NH}_3$  there must be six distinct vibrational modes

## Cartesian representation

- ▶ Consider  $n$  cartesian coordinate systems  $\mathbf{r}_i$  residing on each atom  $i = 1 \dots n$
- ▶ The action of each symmetry operations on each coordinate determines a  $3n$ -dimensional representation  $\Gamma$  of the symmetry group
- ▶ For example,  $C_3$  for  $\text{NH}_3$  is represented by:

$$\mathbf{C}_3 = \begin{bmatrix} \uparrow & \uparrow & \cdots & \uparrow \\ C_3(\hat{\mathbf{x}}_1) & C_3(\hat{\mathbf{y}}_1) & \cdots & C_3(\hat{\mathbf{z}}_n) \\ \downarrow & \downarrow & & \downarrow \end{bmatrix} = \begin{bmatrix} \mathbf{0} & \mathbf{A} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{A} & \mathbf{0} \\ \mathbf{A} & \mathbf{0} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{A} \end{bmatrix}$$

where, for  $\theta = \frac{2\pi}{3}$ ,

$$\mathbf{A} = \begin{bmatrix} \cos \theta & -\sin \theta & 0 \\ \sin \theta & \cos \theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

# Irreducible representations of normal modes

Reduction of  $\Gamma$  using character table of  $\mathcal{C}_{3v}$

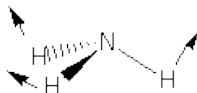
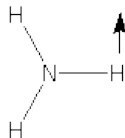
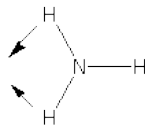
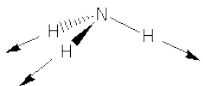
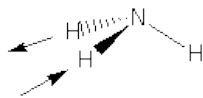
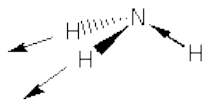
$\mathcal{C}_{3v}$	$E$	$2C_3$	$3\sigma_v$	
$A_1$	1	1	1	$z$
$A_2$	1	1	-1	$R_z$
$E$	2	-1	0	$(x, y), (R_x, R_y)$
$\Gamma$	12	0	2	$\leftarrow$ (traces of $\mathbf{E}, \mathbf{C}_3, \sigma_v$ )

- ▶ Think of rows in the above table as vectors
- ▶ Then  $\Gamma = 3A_1 + A_2 + 4E$
- ▶ But some operations are not proper vibrations! We discard representations corresponding to any of  $x, y, z, R_x, R_y, R_z$  above, retaining  $2A_1 + 2E$

## Interpretation

- ▶ The displacement vectors of normal mode form a basis for one of the irreducible representations  $A_1$  and  $E$
- ▶ For each irreducible representation in each point group, one can deduce (once and for all) whether normal modes belonging to that representation can be infrared or Raman active, or possibly both
- ▶ In our case we know that,  $A_1$  and  $E$  contribute to both, for which reason all six normal modes will contribute to infrared as well as Raman spectra (which makes this a slightly boring result, but such is the price of relative simplicity)
- ▶ This procedure can be performed for any molecule, thus predicting numbers of spectral peaks

# Actual vibrational modes



Lowest two images depict  $A_1$  modes, the remainder are  $E$  modes

Thank you for listening

Incidentally, the Wikipedia article of the day is the one about groups.