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
- These vibrational modes can be characterized by their symmetry properties, each mode “belonging” to an irreducible representation of the system

hello

Example system: NH_3

- Each atom has three positional degrees of freedom, for a total of 12 in the case of NH_3
- Uniform dislocation 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
- Therefore there must be

Cartesian representation

- Consider n cartesian coordinate systems $\mathbf{r}_i$ residing on each atom $i = 1 \ldots n$
- The action of each symmetry operations on each coordinate determines a $3n$-dimensional representation Γ of the symmetry group
- For example, C_3 for NH_3 is represented by:

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

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 Γ using character table of $\mathscr{C}_{3v}$

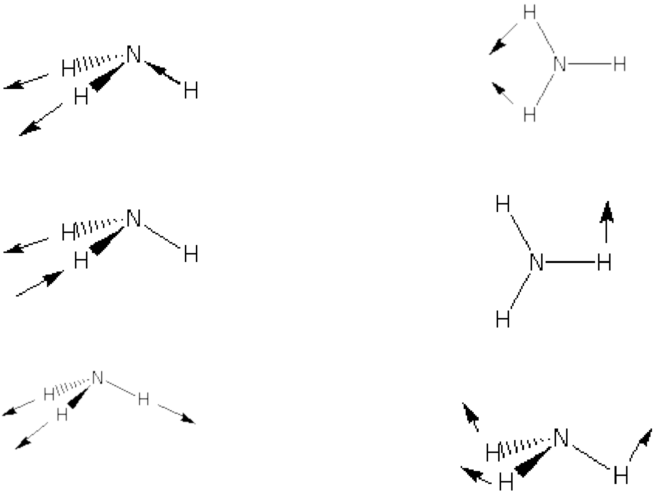
$\mathscr{C}_{3v}$	E	$2C_3$	$3\sigma_v$	
A_1	1	1	1	z
A_2	1	1	-1	R_z
E	2	-1	0	$(x, y), (R_x, R_y)$
Γ	12	0	2	$\leftarrow$ (traces of $\mathbf{E}, \mathbf{C}_3, \boldsymbol{\sigma}_v$)

- 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 are 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.