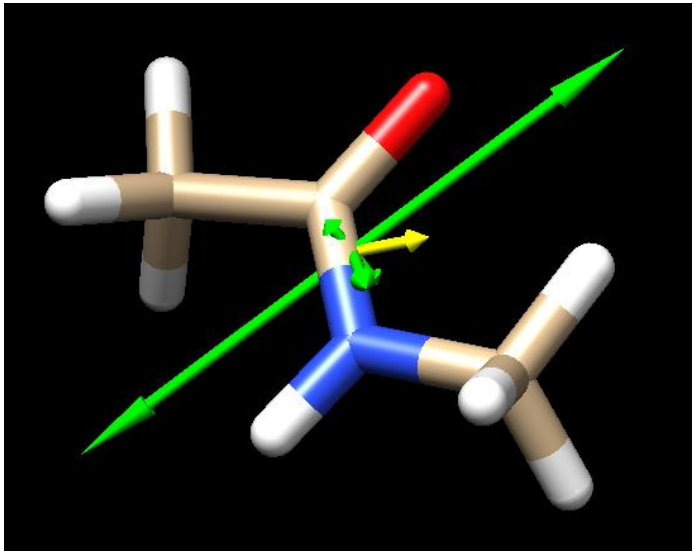
Tensor visualization



Objectives:

1. Coordinate-independent visualization of molecular tensors.

2. Describe sagittary representations for the resonant molecular tensor.

Worked Example

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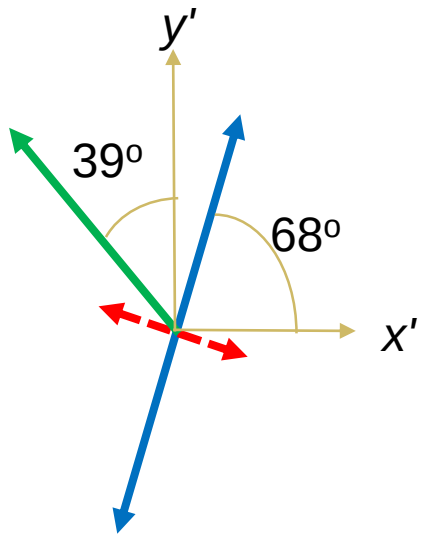
Note: Citations to the contents of these slides should reference the following textbook:
Simpson, Garth J. (2017) *Nonlinear Optical Polarization Analysis in Chemistry and Biology* (Cambridge University Press, ISBN 978-0-521-51908-3).

Example: ir-vis SFG from a planar chromophore

Worked example. What are the nonzero tensor elements for this transition?



0.1 e·a_0

0.2 $e^2 \cdot a_0^2 \cdot E_h^{-1}$

First, the transition moment

$$\bar{\mu} = 0.13 e a_0 \begin{bmatrix} -\sin(39^0) \\ \cos(39^0) \end{bmatrix} = \begin{bmatrix} -0.08 \\ 0.101 \end{bmatrix} e a_0$$

To generate α in the reference (x',y') coordinate system, first define it in the principal coordinate system (x_0,y_0) then rotate.

$$\bar{\alpha}' = \left(0.2 e^2 a_0^2 E_h^{-1}\right) R(68^0) \otimes R(68^0) \begin{bmatrix} 2.40 \\ 0 \\ 0 \\ -0.90 \end{bmatrix} = \begin{bmatrix} -0.09 \\ 0.229 \\ 0.229 \\ 0.387 \end{bmatrix} e^2 a_0^2 E_h^{-1}$$

Now combine.

$$\vec{\beta} = S(\omega_{ir})\,\bar{\alpha} \otimes \bar{\mu} = S(\omega_{ir}) \begin{bmatrix} 0.007 \\ -0.019 \\ -0.019 \\ -0.032 \\ -0.009 \\ 0.023 \\ 0.023 \\ 0.039 \end{bmatrix} e^3 a_0^3 E_h^{-1}$$

$\beta_{x'x'x'}$

$\beta_{y'y'y'}$

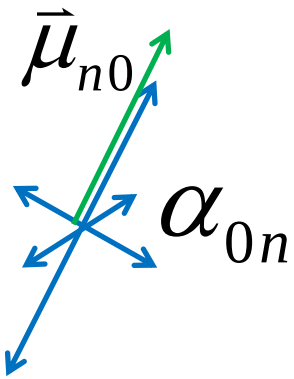
Perry, J.M.; Moad, A.J.; Begue, N.J.; Wampler, R.D.; Simpson, G.J. *J. Phys. Chem. B, 109,* **2005**,20009-20026.

Garth J. Simpson

I. Sagittary representations of the resonant molecular tensor

Limitations of the sagittary representations.

Resonant SFG.



This representation ONLY works well for individual chromophores and individual exciton transition, but cannot be trivially generalized to represent the NLO properties of weakly coupled ensembles.

$$\beta_{res}^{(2)} = S_n\left(\omega_{ir}\right)\alpha_{0n} \otimes \mu_{n0}$$

NLOPredict

http://nlopredict.sourceforge.net/

Tensor visualization, rotation, and manipulation software package based on the mathematical framework described in this meeting.

- Performs evaluation of the local-frame and ensemble-frame responses as a function of orientation.
- Incorporates all the visualization techniques described in this presentation for both single molecules and ensembles (where appropriate).
- Open-source software available through Sourceforge.net.
- Piggybacks as an add-in to the protein visualization package UCSF Chimera (http://www.cgl.ucsf.edu/chimera/).

Moad, A.J.; Moad, C.W.; Perry, J.M.; Wampler, R.D.; Goeken, G.S.; Begue, N.J.; Shen, T.; Heiland, R.; Simpson, G.J. *J. Comput. Chem*. **2007,** *28*,1996-2002.

Summary

I. Sagittary representations

Pros:

i) intuitive and rigorously complete when coupled with the lineshape function,

ii) invertible to numerically recover the complete molecular tensor in any reference frame.

Cons:

i) only applicable to individual transitions and not ensembles,

ii) does not include the nonresonant contributions.