Tensor visualization

Objectives:
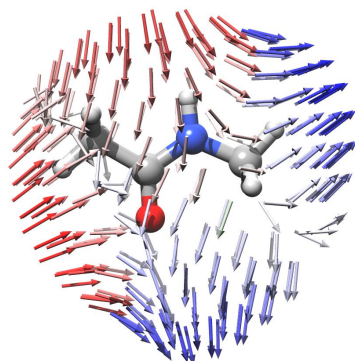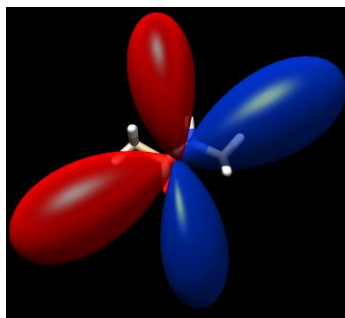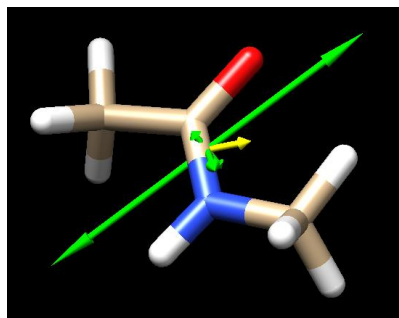
1. Coordinate-independent visualization of molecular tensors.

2. Describe sagittary representations for the resonant molecular tensor.

Garth J. Simpson

**Department of Chemistry
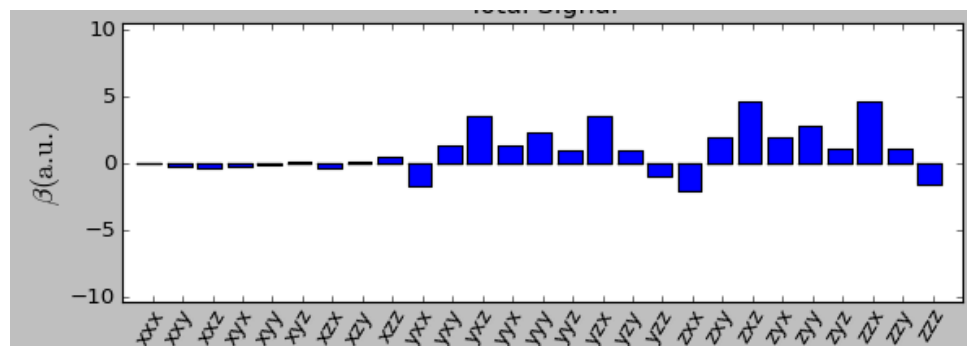Purdue University**

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Visual representations

Numerical representation

Computational chemistry typically produces outputs as tables of 18 or 27 numbers.

1. It can be difficult to connect these numbers to particular molecular structural motifs.
2. For a particular vibrational transition, the coordinate system of the molecule will generally be different that the local mode of the transition of interest.
3. Very different sets of tensor elements are recovered depending on the particular choice of the internal molecular coordinates selected.
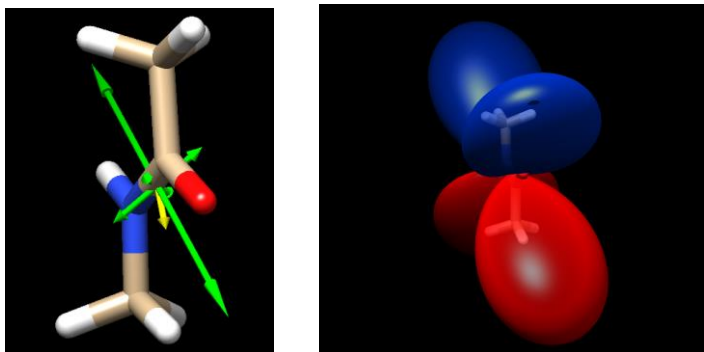

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Visual representations

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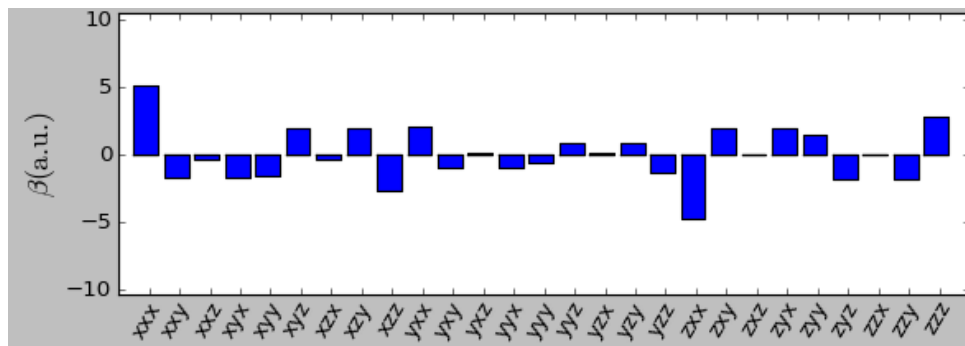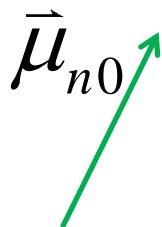
Numerical representation

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Transition moment.

$$\vec{\mu}_{n0}$$

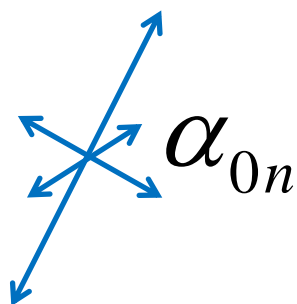Each one-photon resonance that collectively contributes to the linear polarizability is described by a transition moment, which is a vector property in the molecule.

The linear polarizability matrix is constructed by the Kronecker product of the transition moment with its transposed conjugate.
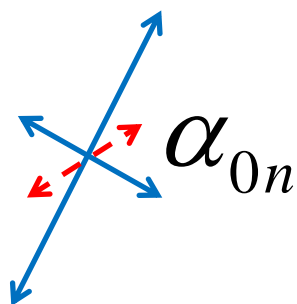
Perry, J.M.; Moad, A.J.; Begue, N.J.; Wampler, R.D.; Simpson, G.J. *J. Phys. Chem. B, 109,* **2005,**20009-20026.

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Chautauqua

Raman polarizability.

$$\alpha_{0n}$$

The Raman tensor is a 3×3 matrix. As long as the virtual states in the Raman process are far from resonance (i.e., adiabatic limit), the tensor is symmetric Just like the moment of inertia matrix, the symmetric Raman tensor can be described by three principal eigenvectors and their corresponding eigenvalues. In this reference frame, only the three diagonal elements within the Raman matrix are nonzero.

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

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Raman polarizability.

Red, dashed lines indicate principal Raman elements with negative sign.

Solid, blue lines indicate positive sign.

$$\alpha_{0n}$$

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

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Vibrationally Resonant SFG.

$$\vec{\mu}_{n0}$$

$$\alpha_{0n}$$

The combined representations for the transition moment and Raman tensor together with the assumed complex-valued lineshape function recover the resonant contributions to the molecular tensor in any arbitrary coordinate system.

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

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

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Electronically Resonant SHG.

$$\vec{\mu}_{n0}$$

$$\alpha_{0n}$$

The combined representations for the transition moment and **TPA** tensor together with the assumed complex-valued lineshape function recover the resonant contributions to the molecular tensor in any arbitrary coordinate system.
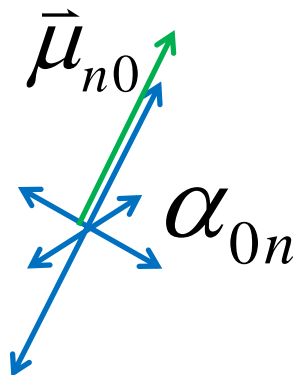
$$\beta_{res}^{ijk} = S_n\left(2\omega\right)\mu_{0n}^{i} \otimes \alpha_{n0}^{jk}$$

Lineshape resonance about 2ω instead of ω_{ir}.

Order flips relative to vib. SFG

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