Effect of spatial symmetry on $\chi^{(n)}$

Nonlinear Optics
Lecture 3

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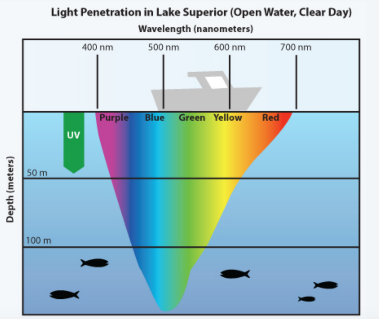
Take H_2O: dispersionless vs. lossless

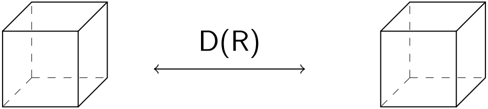


Minnesota Sea Grant, 2012

- When to use Kleinmanns symmetry or consider lossless material $\rightarrow$ matter of choice
- Be aware of neglected effects:
  - Weak overtones provide some absorption (lossless)
  - Refractive index is wavelength dependent n(λ) (dispersionless)

Spatial symmetry - effects on $\chi^{(n)}$

Neumanns symmetry principle: every tensor that describes a physical property of the material must be invariant under the symmetry operations that describe the spatial symmetry of the material



$$\chi^{(n)}(\text{after R}) = \chi^{(n)}(\text{before R})$$

R ... symmetry operation
D(R) ... representation of R

Operations

E … identity operator $\quad D(E) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$

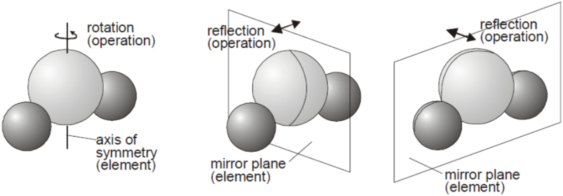
i … inversion operator $\quad D(i) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$

σ … reflection on a plane $\quad D(\sigma_{xy}) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$

$$D(\sigma_{xz}) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad D(\sigma_{yz}) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

C_n ... rotation $\quad D(C_n)_z = \begin{pmatrix} \cos(\phi) & \sin(\phi) & 0 \\ -\sin(\phi) & \cos(\phi) & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \phi = \frac{360^\circ}{n}$

S_n ... improper rotation $\quad D(S_n)_z = \begin{pmatrix} \cos(\phi) & \sin(\phi) & 0 \\ -\sin(\phi) & \cos(\phi) & 0 \\ 0 & 0 & -1 \end{pmatrix}$



Chemical Libretexts, Oxford University 2017

Neumanns symmetry for $\chi^{(1)}$-, $\chi^{(2)}$-, $\chi^{(3)}$-tensor

Simliarity transformations using the Einstein summation convention:

$$\chi_{ij}^{(1)*} = \sum_{l,m} D_{il}^T \chi_{lm}^{(1)} D_{mj} = D_{li} \chi_{lm}^{(1)} D_{mj}$$

$$\chi_{lmn}^{(2)*} = \sum_{i,i,k} D_{li}^T \chi_{ijk}^{(2)} D_{jm} D_{kn} = D_{il} \chi_{ijk}^{(2)} D_{jm} D_{kn}$$

$$\chi_{pqrs}^{(3)*} = \sum_{i,j,k,l} D_{pi}^T \chi_{ijkl}^{(3)} D_{jq} D_{kr} D_{ls} = D_{ip} \chi_{ijkl}^{(3)} D_{jq} D_{kr} D_{ls}$$

example: non-zero $\chi^{(1)}$ elements for monoclinic crystal

- If we have multiple R's we have to consider all the D(R) on $\chi^{(1)}$
- Symmetry elements for monoclinic crystal: C_2

Method 1: matrix multiplication:

$$\chi^{(1)} \cdot D(C_2) = \begin{pmatrix} \chi_{11} & \chi_{12} & \chi_{13} \\ \chi_{21} & \chi_{22} & \chi_{23} \\ \chi_{31} & \chi_{32} & \chi_{33} \end{pmatrix} \cdot \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$= \begin{pmatrix} -\chi_{11} & -\chi_{12} & \chi_{13} \\ -\chi_{21} & -\chi_{22} & \chi_{23} \\ -\chi_{31} & -\chi_{32} & \chi_{33} \end{pmatrix}$$

$$D^T(C_2) \cdot \chi^{(1)} \cdot D(C_2) = \begin{pmatrix} \chi_{11} & \chi_{12} & -\chi_{13} \\ \chi_{21} & \chi_{22} & -\chi_{23} \\ -\chi_{31} & -\chi_{32} & \chi_{33} \end{pmatrix}$$

nonzero: $\chi_{11}, \chi_{12}, \chi_{21}, \chi_{22}, \chi_{33}$; zero: $\chi_{31}, \chi_{32}, \chi_{13}, \chi_{23}$

Method 2: Quicker way to obtain result

- Use the fact that D(R) has many zeros!

→ only take D(R) matrix elements that are non-zero and therefore contribute $D_{11} = D_{22} = -1; \quad D_{33} = 1$

$$\begin{aligned}\chi_{11}^{(1)*} = D_{1l}^T \chi_{lm}^{(1)} D_{m1} = D_{11}^T \cdot (\chi_{11} D_{11} + \chi_{12} D_{21} + \chi_{13} D_{31}) \\ + D_{12}^T \cdot (\chi_{21} D_{11} + \ldots) \\ + D_{13}^T \cdot (\ldots) \\ = D_{11} \chi_{11} D_{11} = (-1) \cdot \chi_{11} \cdot (-1) = \chi_{11}\end{aligned}$$

$$\chi_{22}^{(1)*} = D_{22} \chi_{22} D_{22} = (-1) \cdot \chi_{22} \cdot (-1) = \chi_{22}$$
$$\chi_{12}^{(1)*} = D_{11} \chi_{12} D_{22} = (-1) \cdot \chi_{12} \cdot (-1) = \chi_{12}$$
$$\chi_{13}^{(1)*} = D_{11} \chi_{13} D_{33} = (-1) \cdot \chi_{13} \cdot (1) = -\chi_{13}$$

etc. → nonzero: $\chi_{11}, \chi_{12}, \chi_{21}, \chi_{22}, \chi_{33}$; zero: $\chi_{31}, \chi_{32}, \chi_{13}, \chi_{23}$

Recipe to determine non-zero $\chi^{(n)}$ elements

- What are the symmetry operations (Elements R in table)
- Matrices D(R)
- non-zero $D_{ij}(R)$
- examine Neumanns principle for each R
- find allowed/forbidden $\chi^{(n)}$ elements or possible equalities