Molecules and Light

(or, Why you see what you see)

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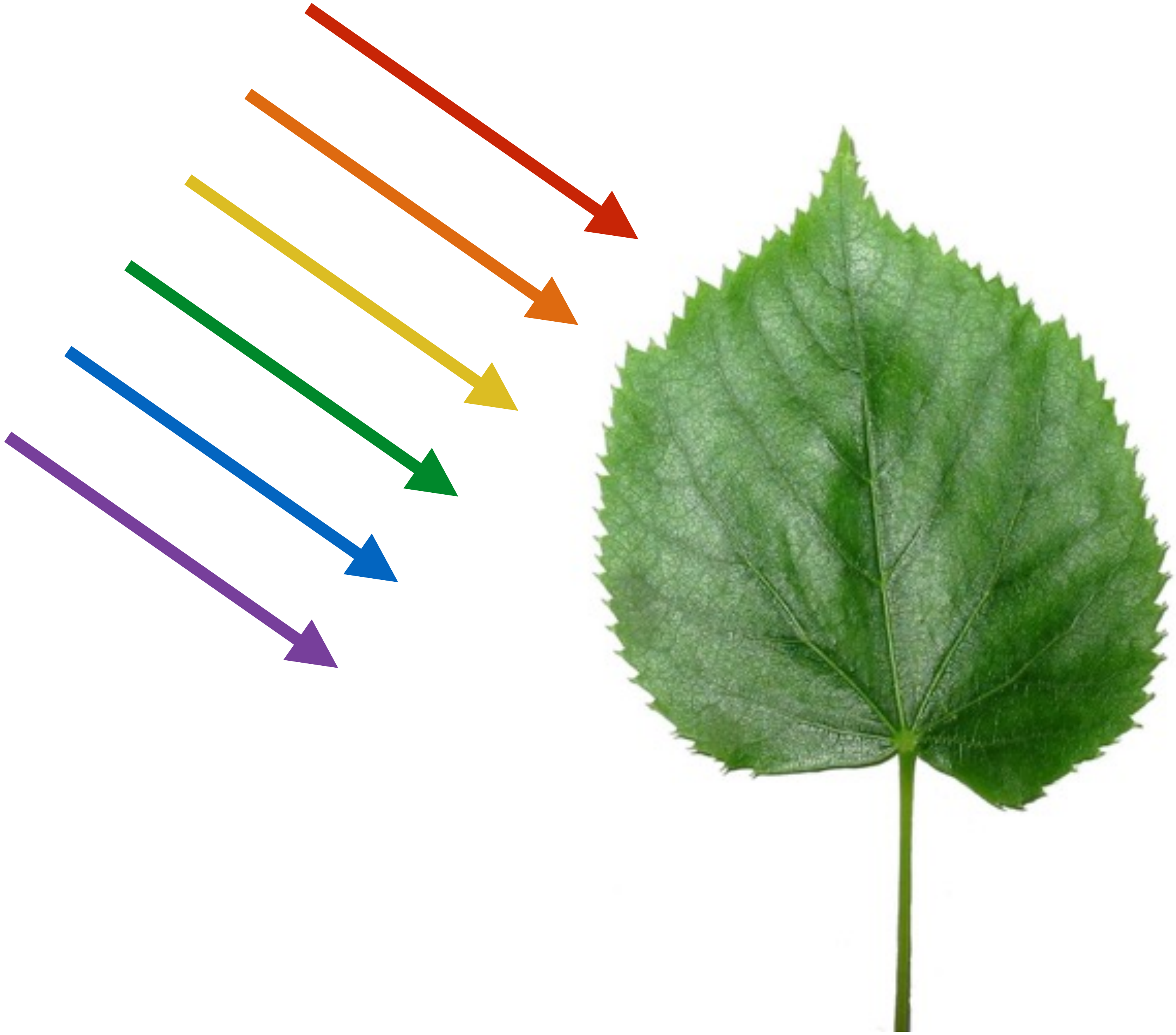
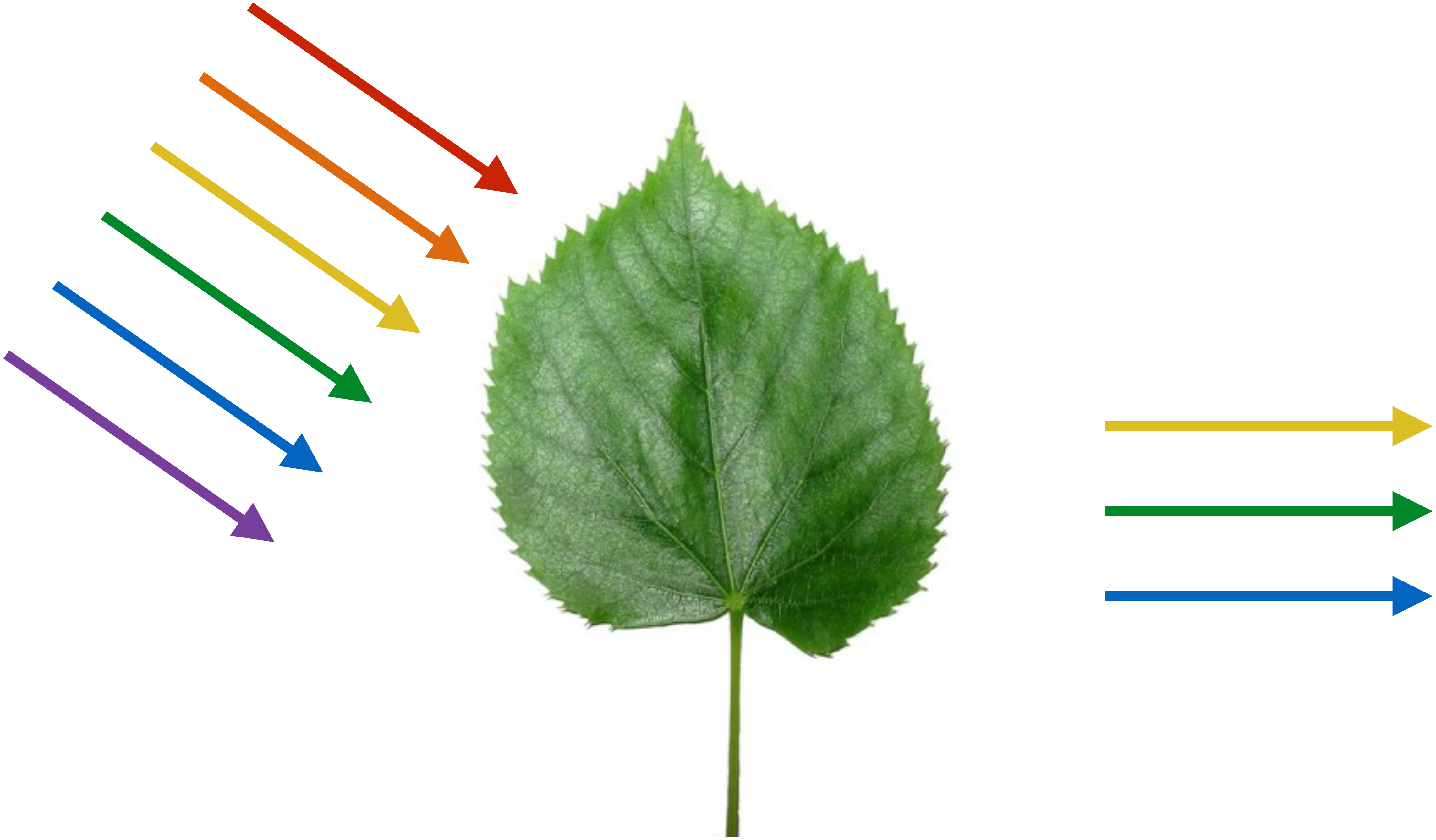
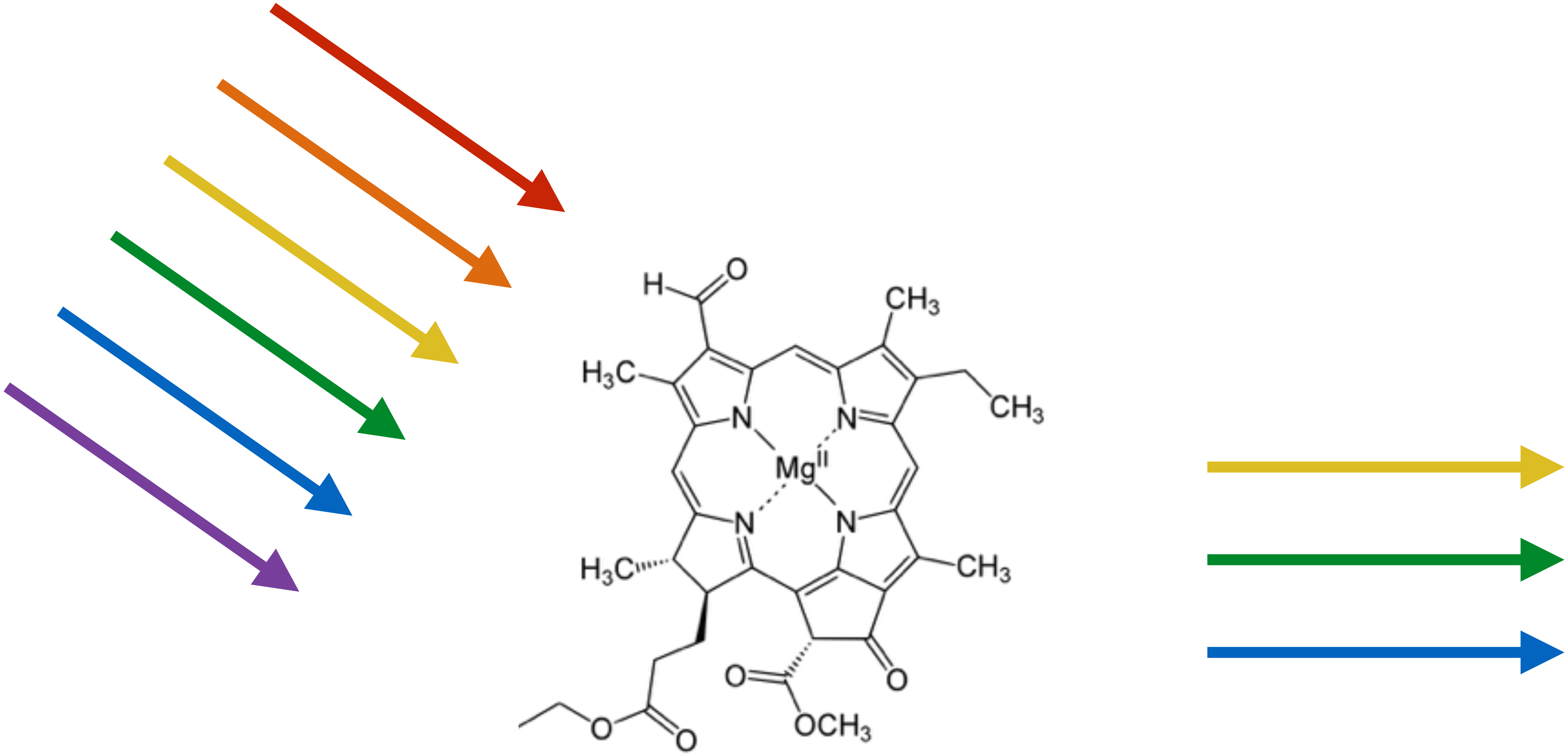
May 2, 2016

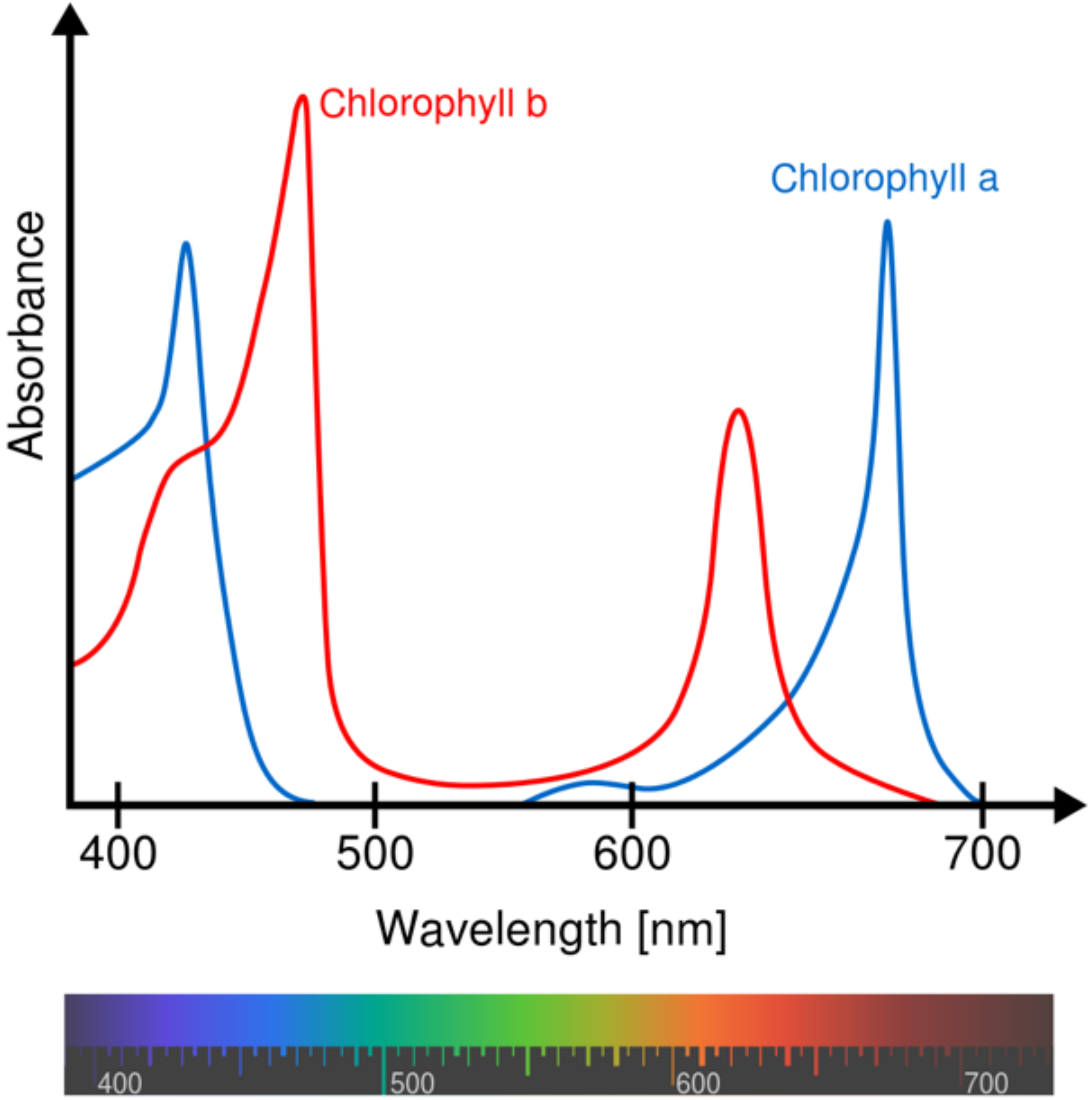
UNIVERSITY *of* WASHINGTON



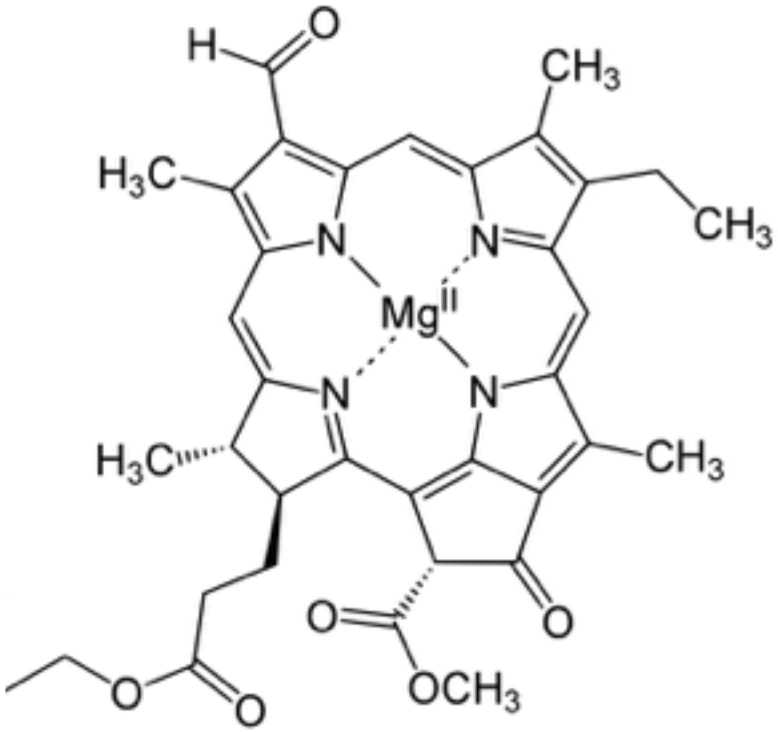




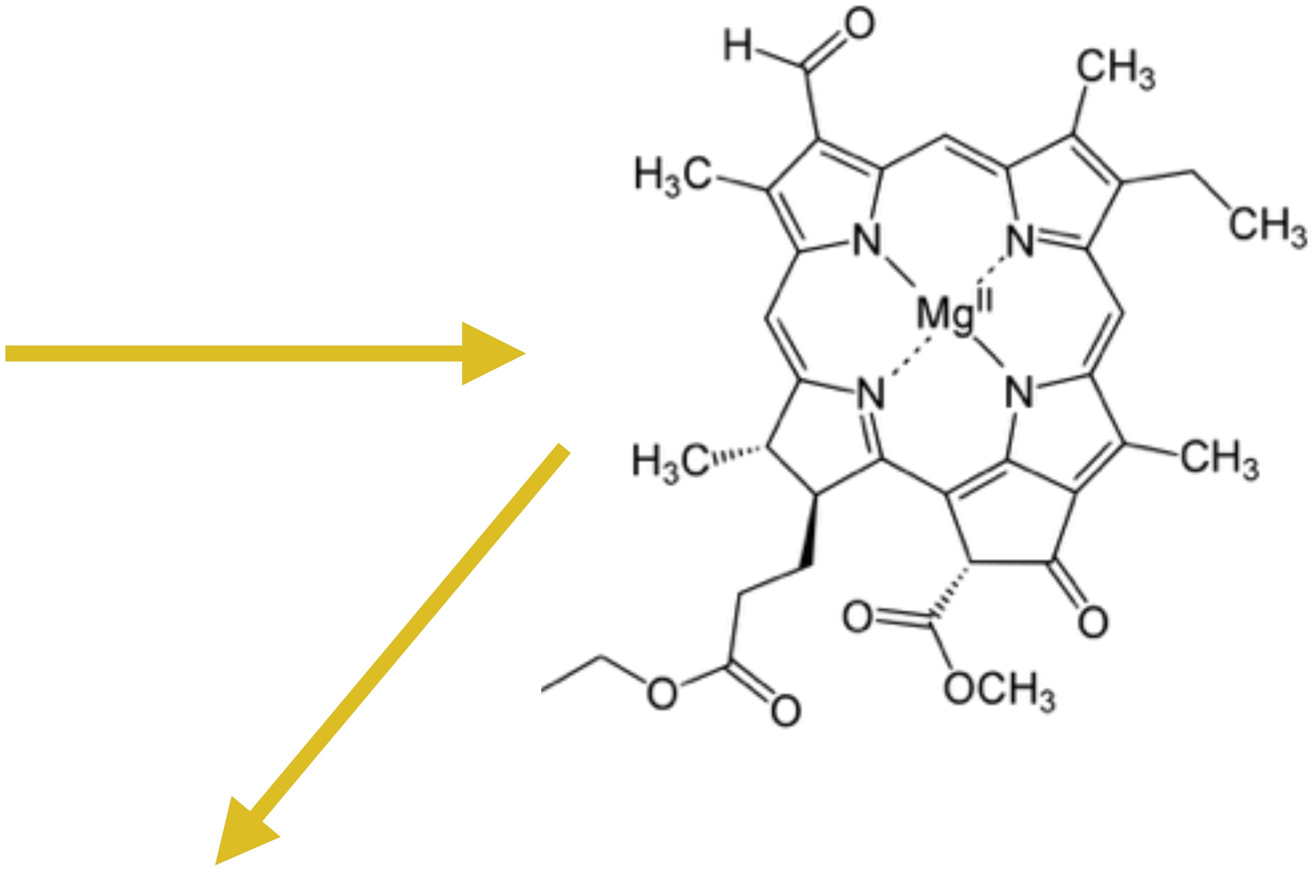
Chlorophyll chromophore


Chlorophyll b
Chlorophyll a
Absorbance
400
500
600
700
Wavelength [nm]
400
500
600
700

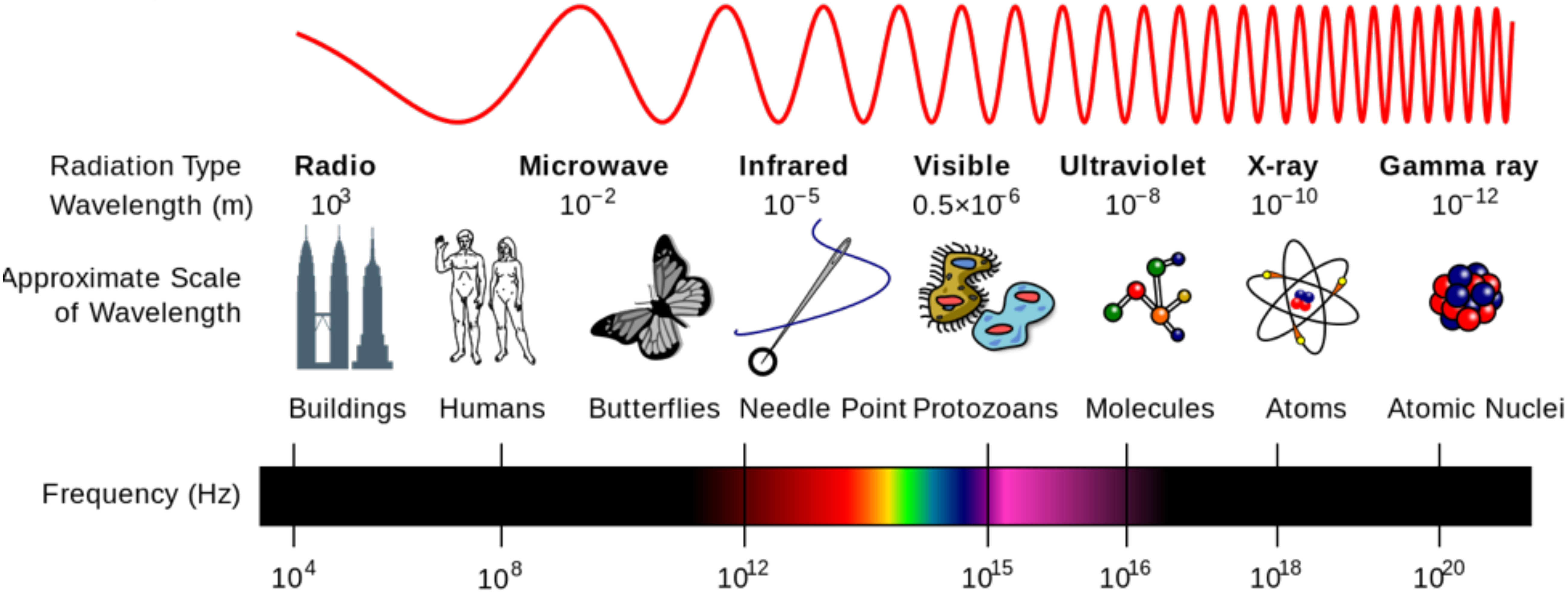
What actually happens when molecules interact with light?



Light doesn’t just “bounce off” molecules.

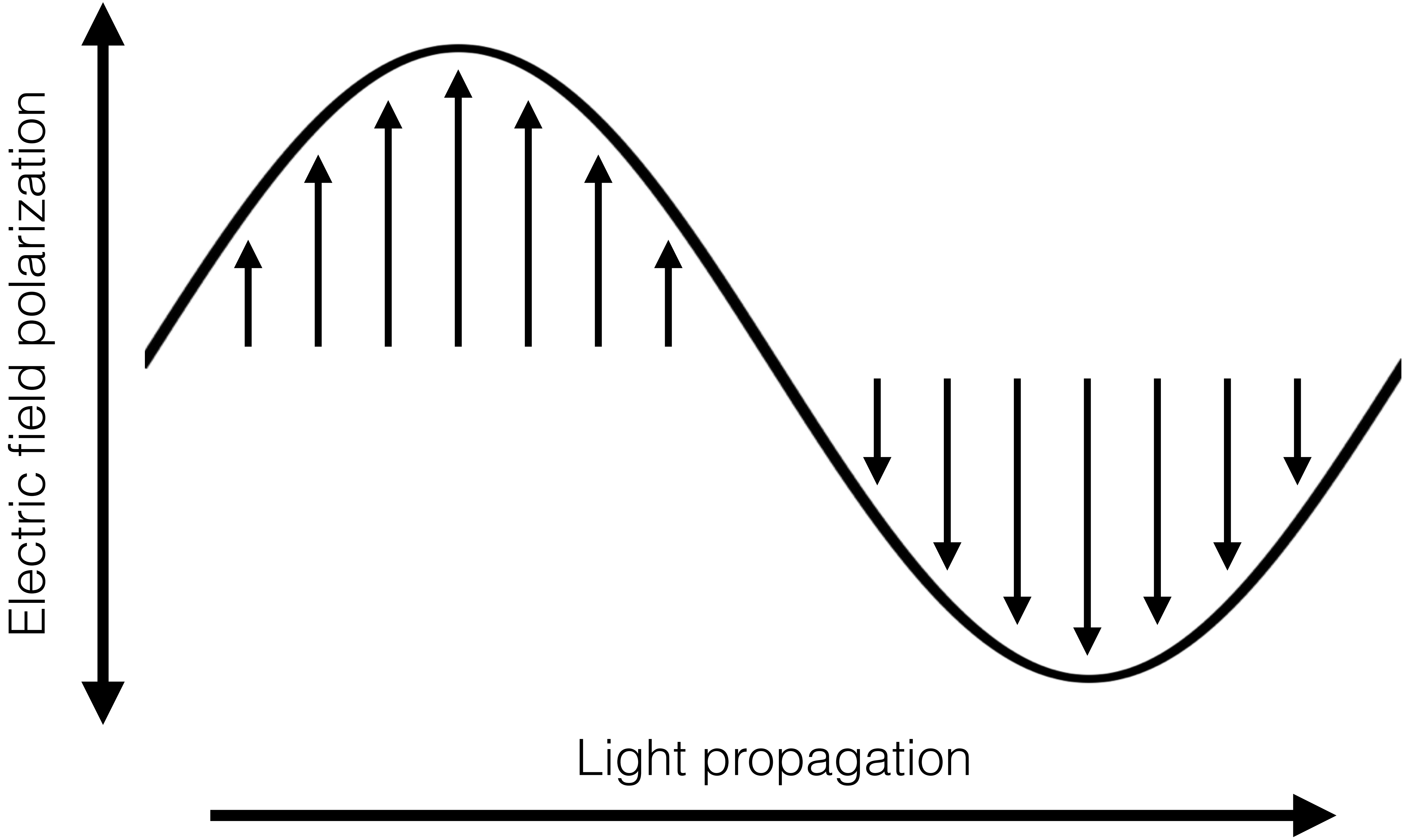


Remember light is really an oscillating electromagnetic field

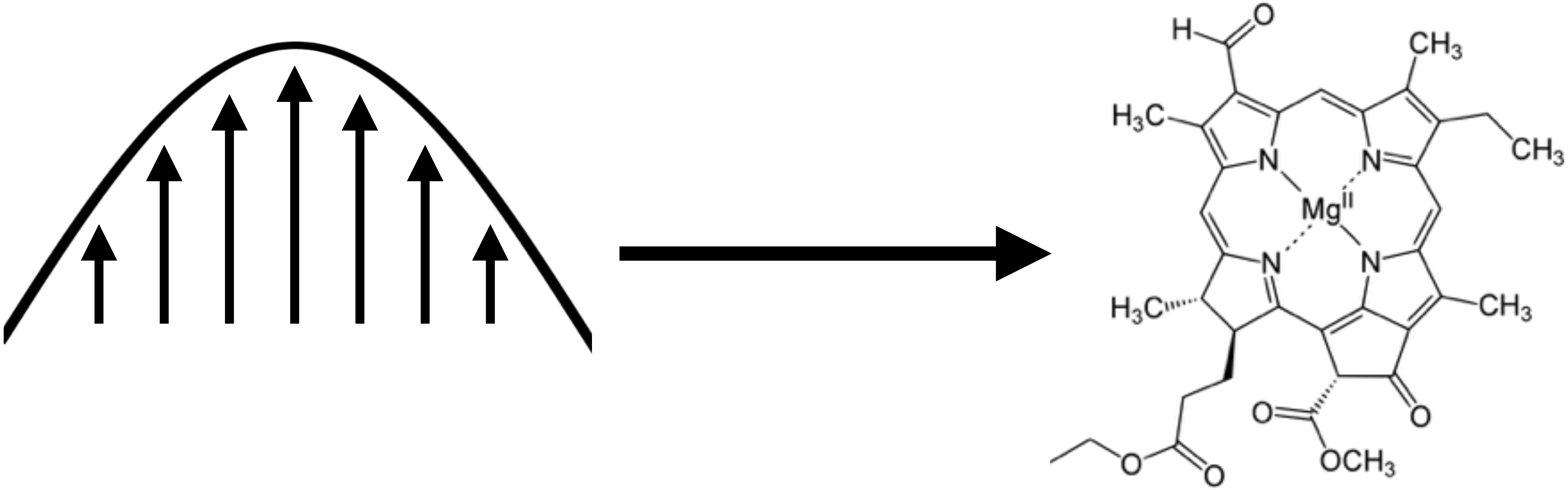


By Inductiveload, NASA CC-BY-SA-3.0, via Wikimedia Commons

Light polarizes charges in a molecule



When light passes over a molecule



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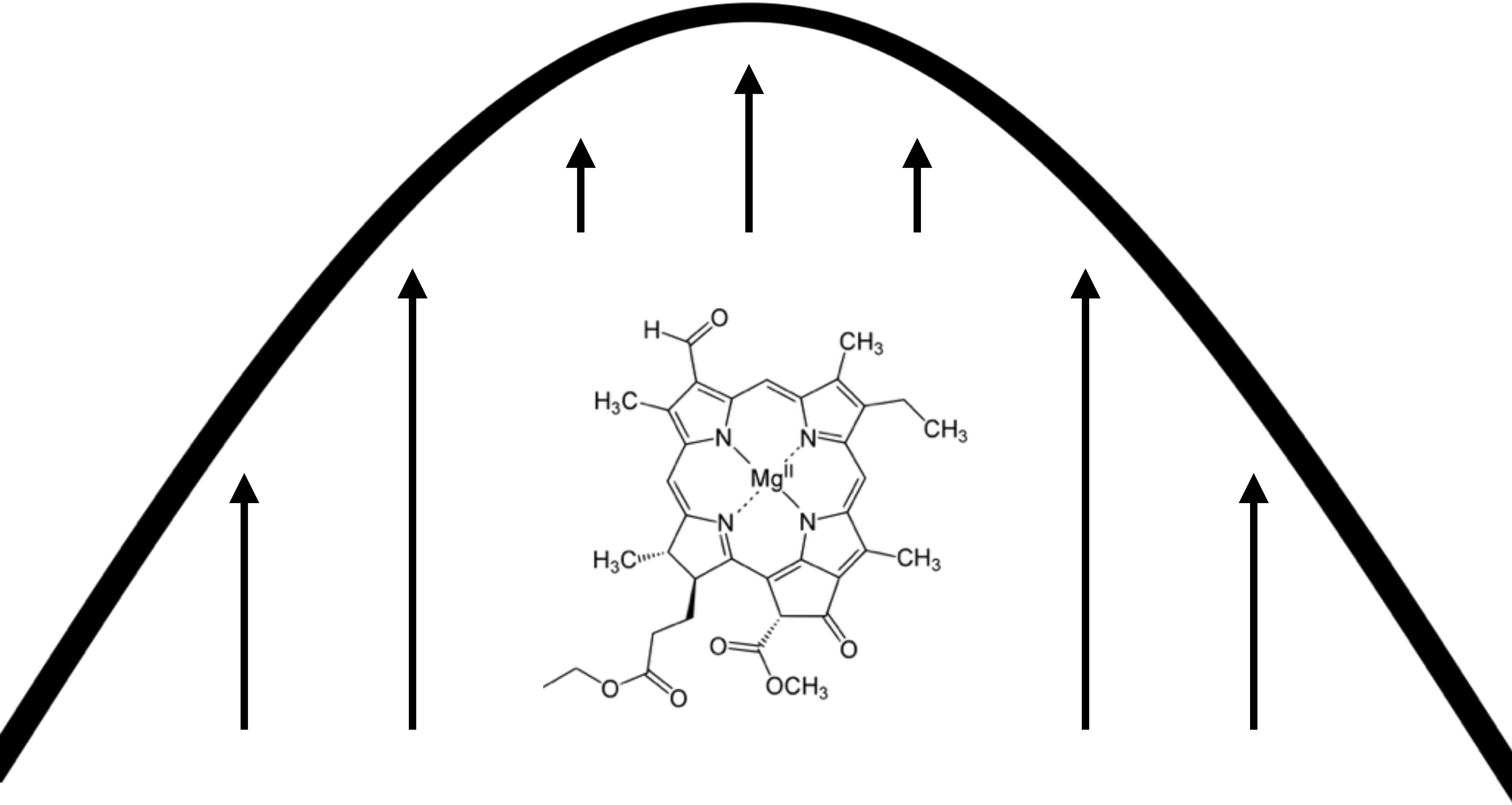

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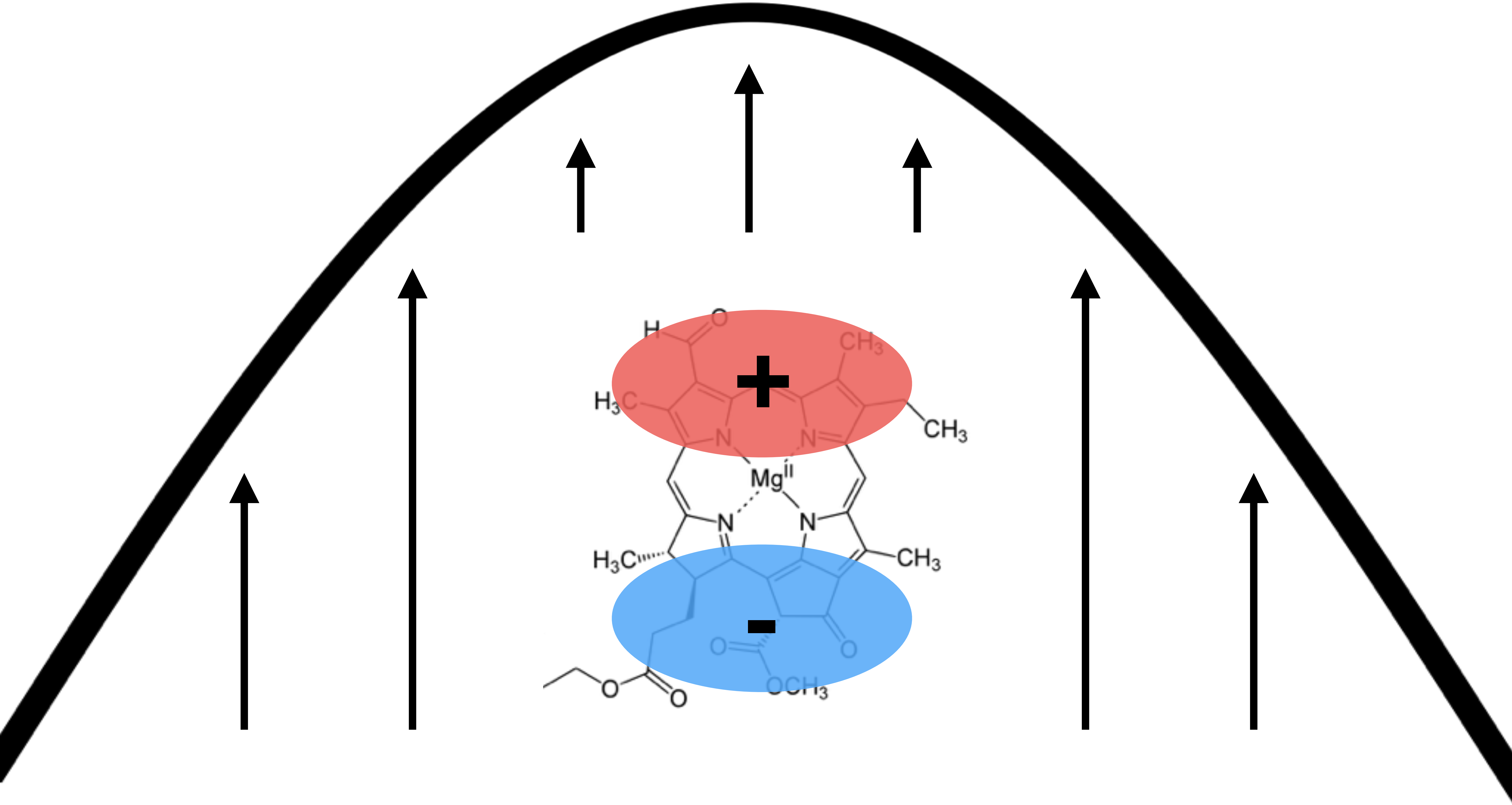
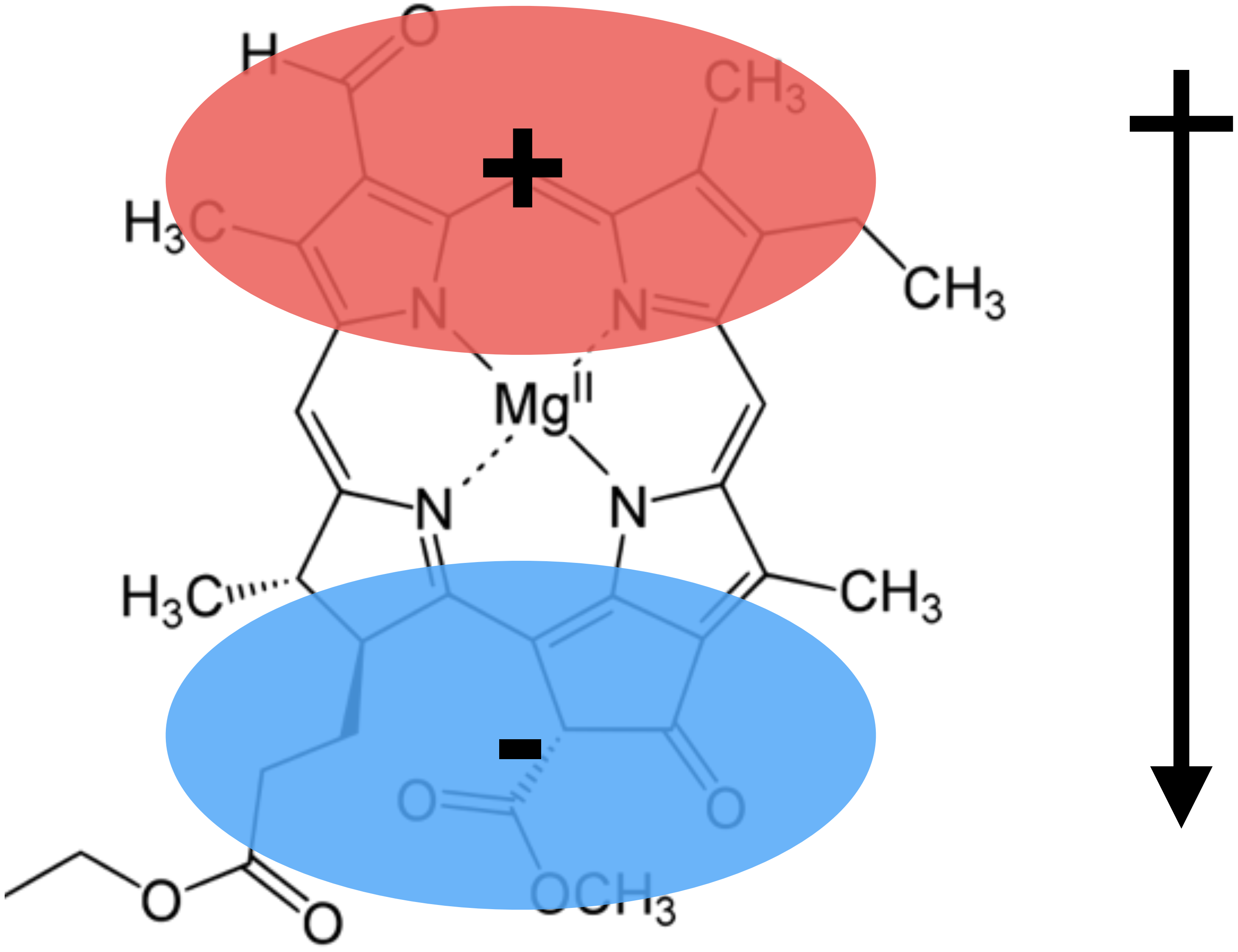
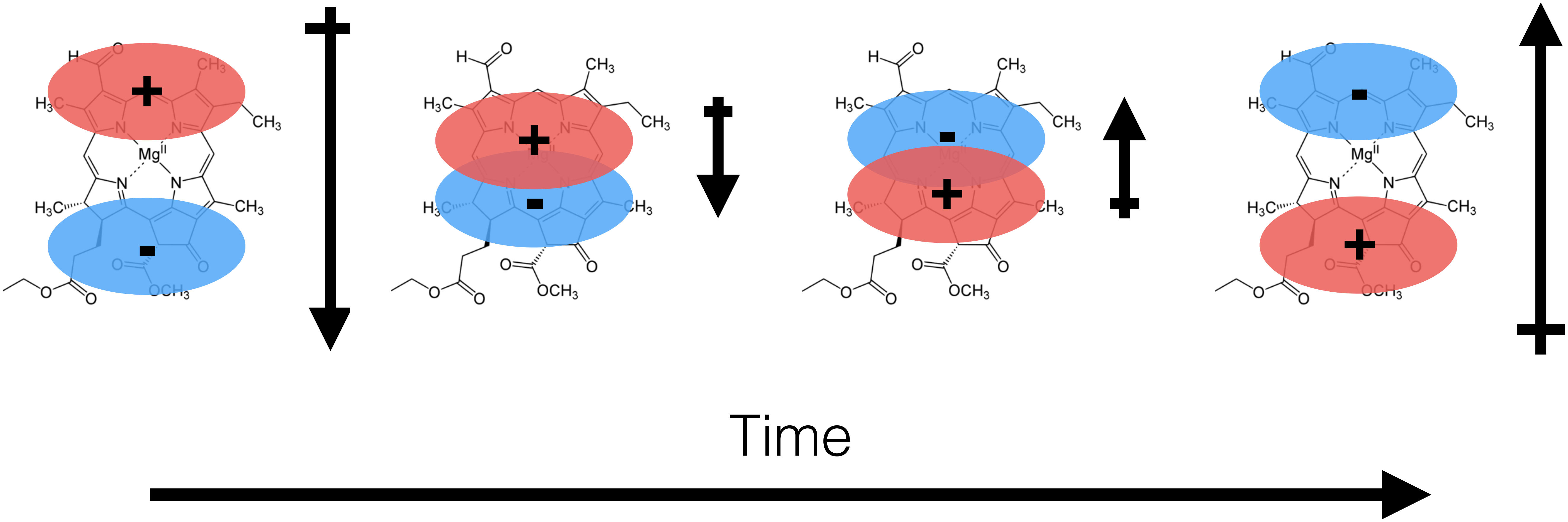


Light induces a dipole moment

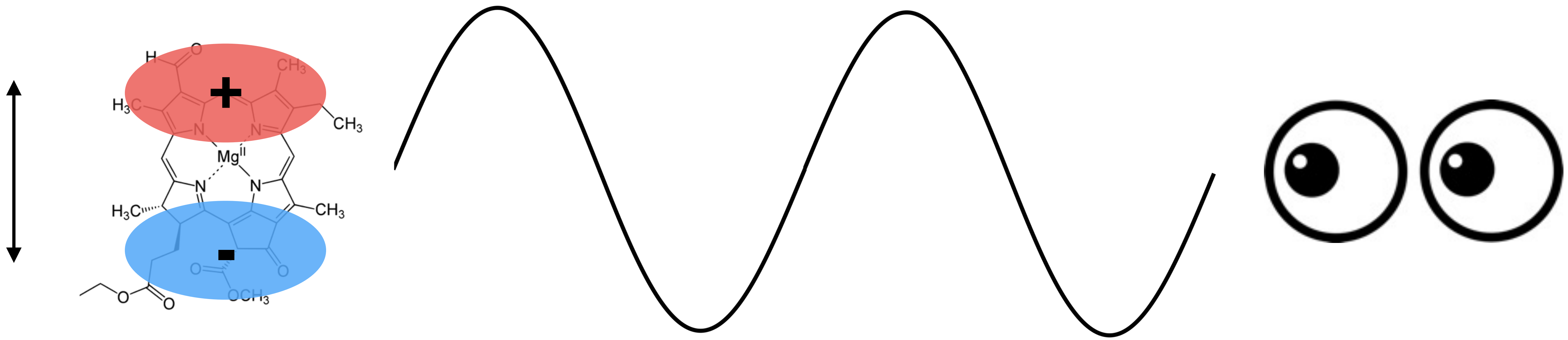
When light passes over a molecule



Light induces a dipole moment

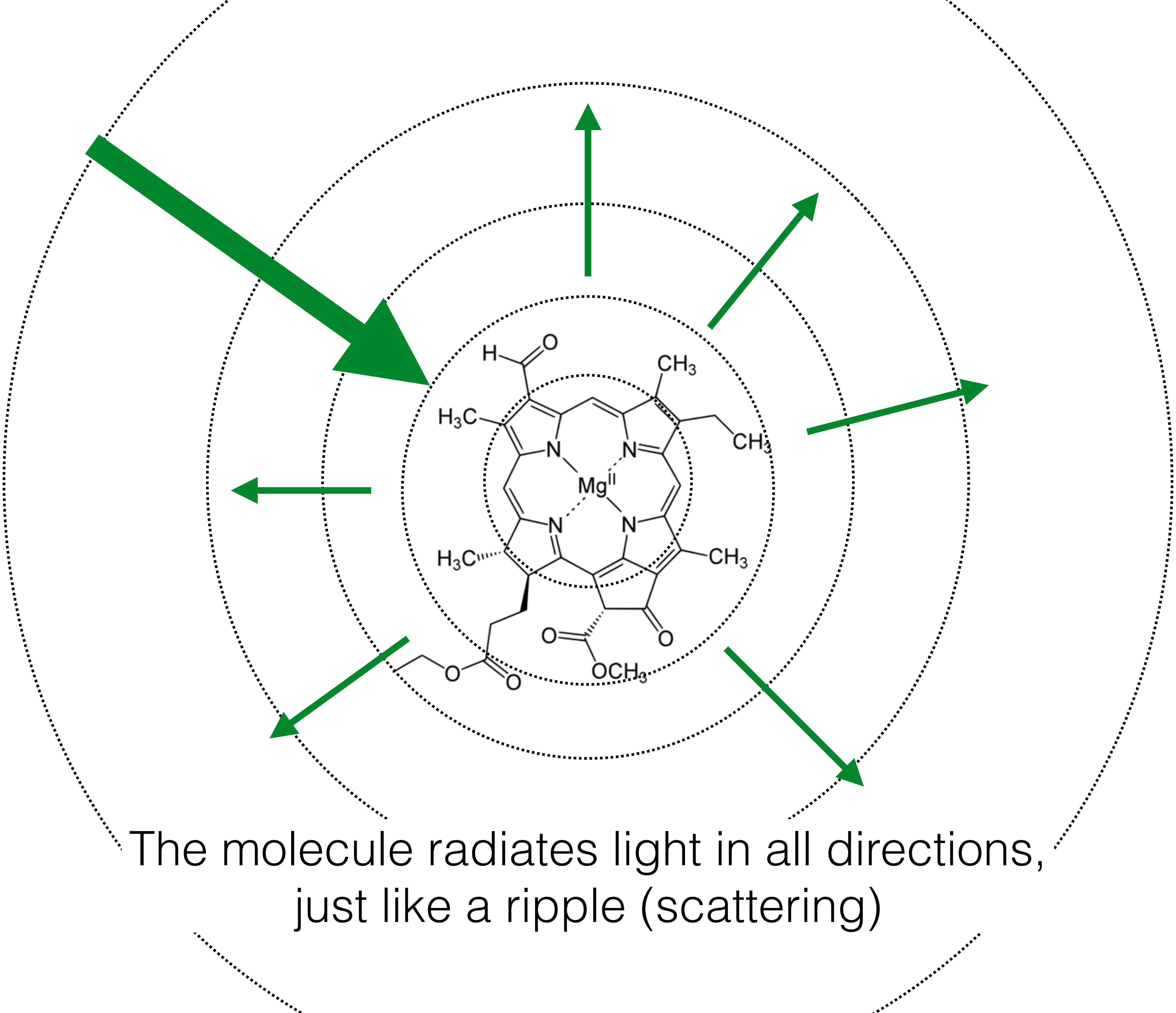


The induced dipole moment oscillates



Oscillating charges give off their own light

This is the reflected (scattered) light you see



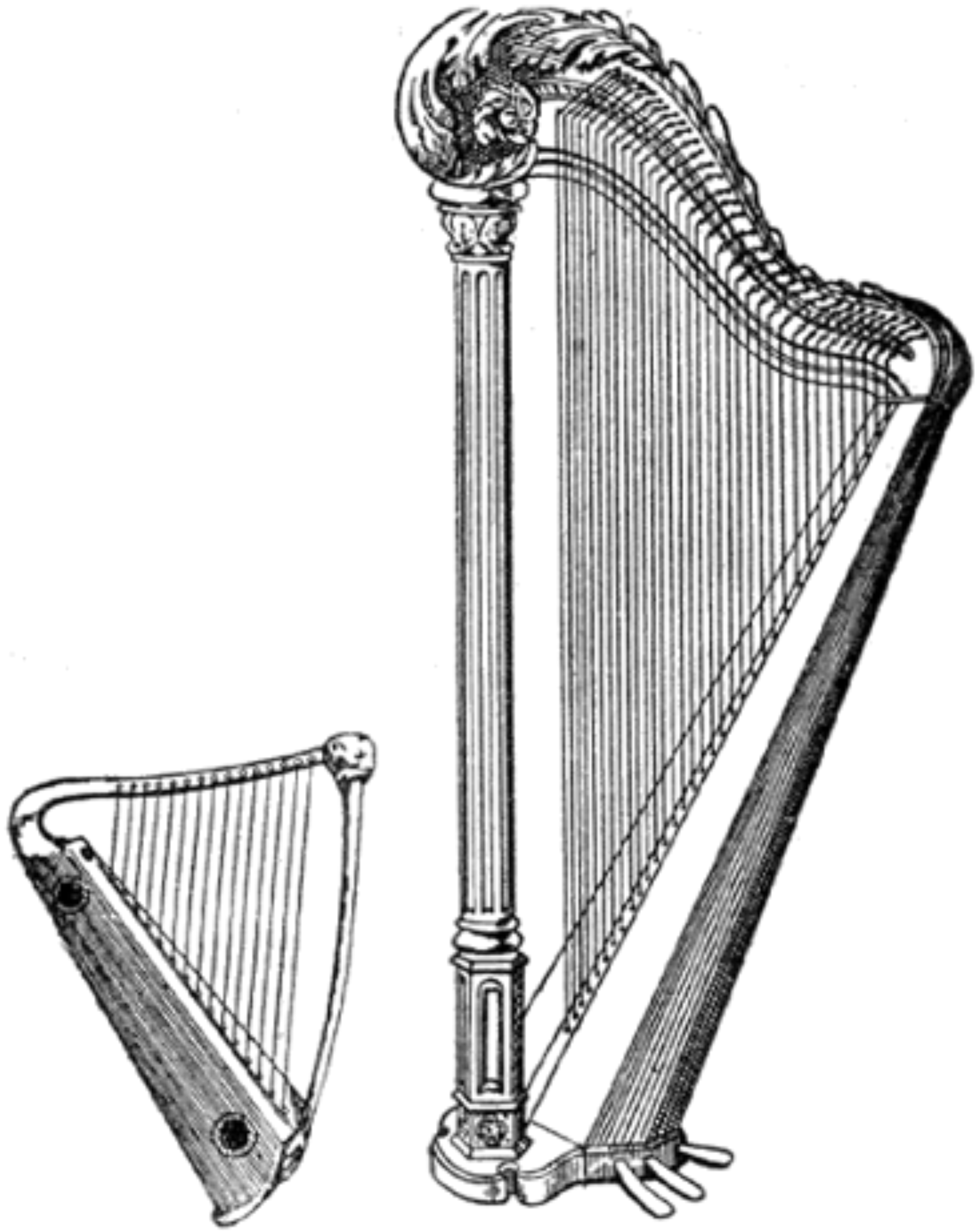
The molecule radiates light in all directions,
just like a ripple (scattering)

So what about absorption?

Think of a harp

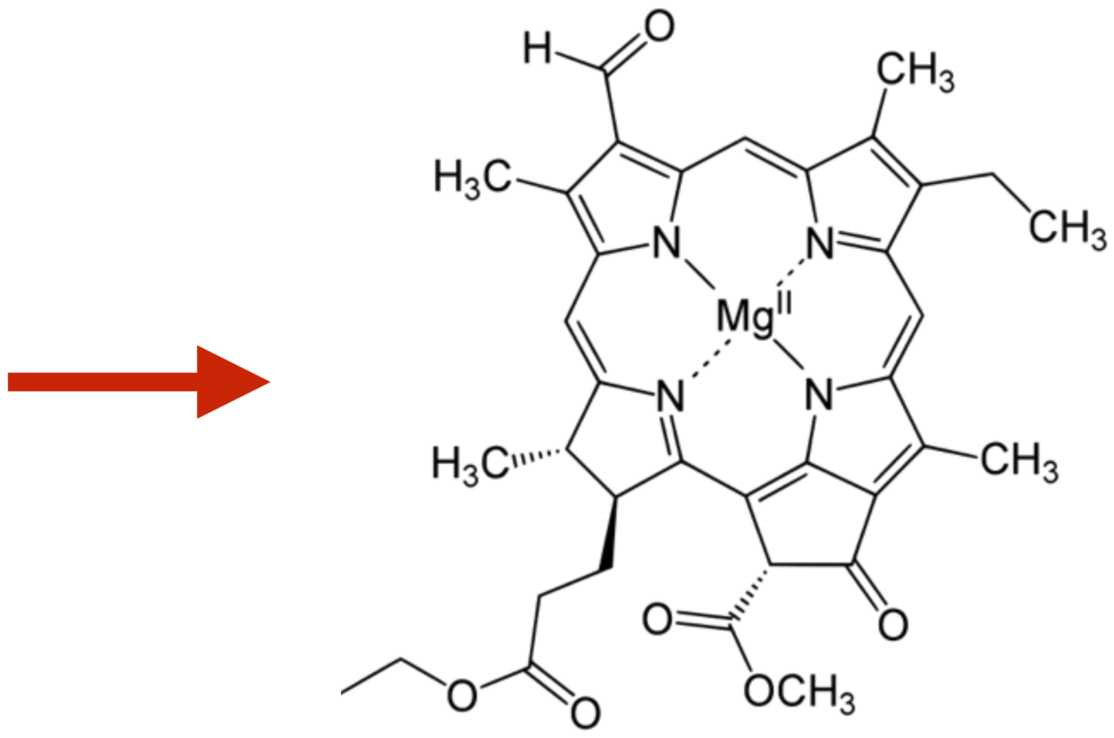
Each length of string has a characteristic note

Every molecule and material has characteristic resonances



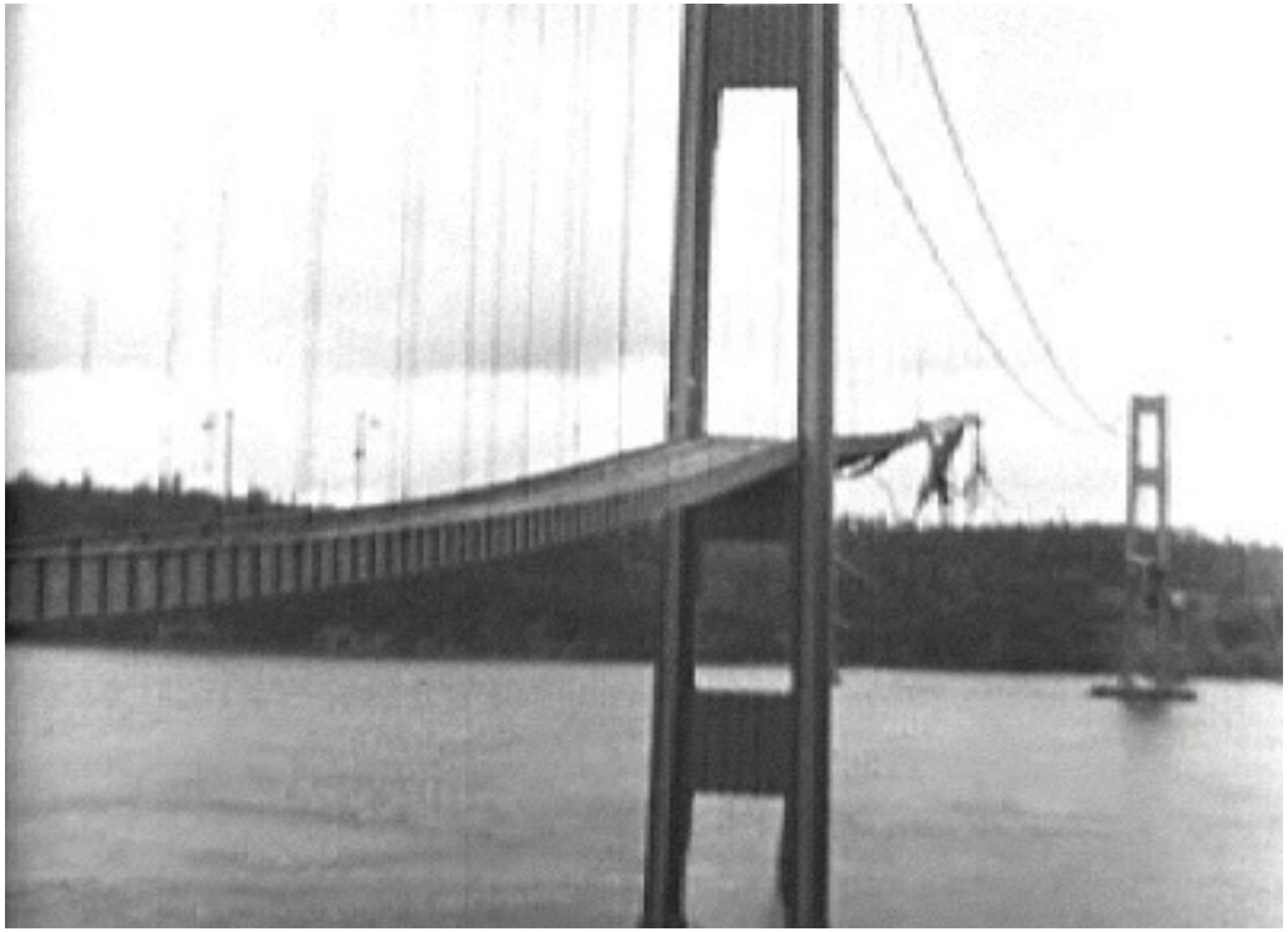
Harps, p. 984.

When a molecule is irradiated by light matching its characteristic resonances, there is a chance it will absorb that light

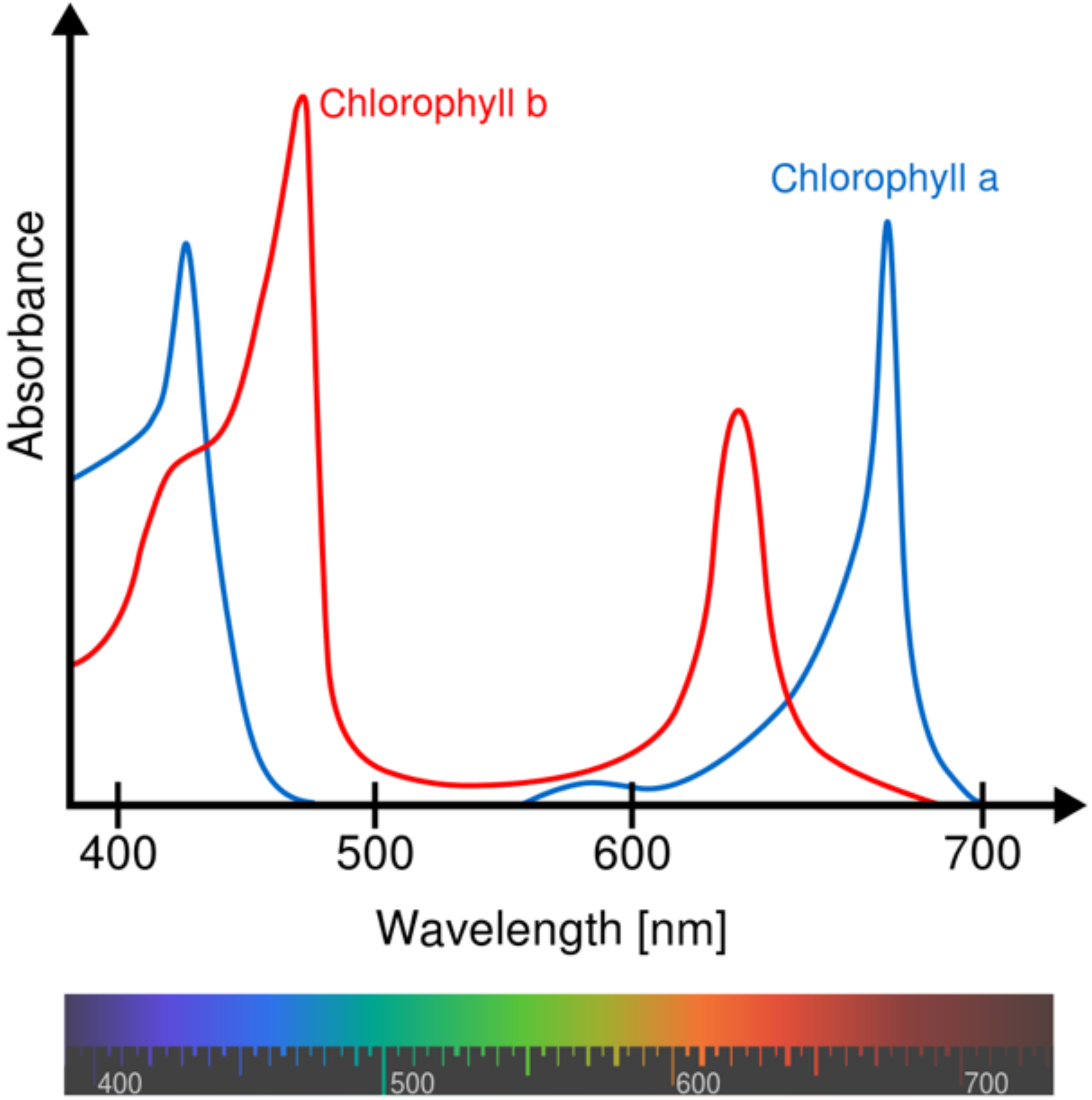


This is energy transfer

Loose analogy: Tacoma Narrows bridge (1940)



https://youtu.be/XggxeuFDaDU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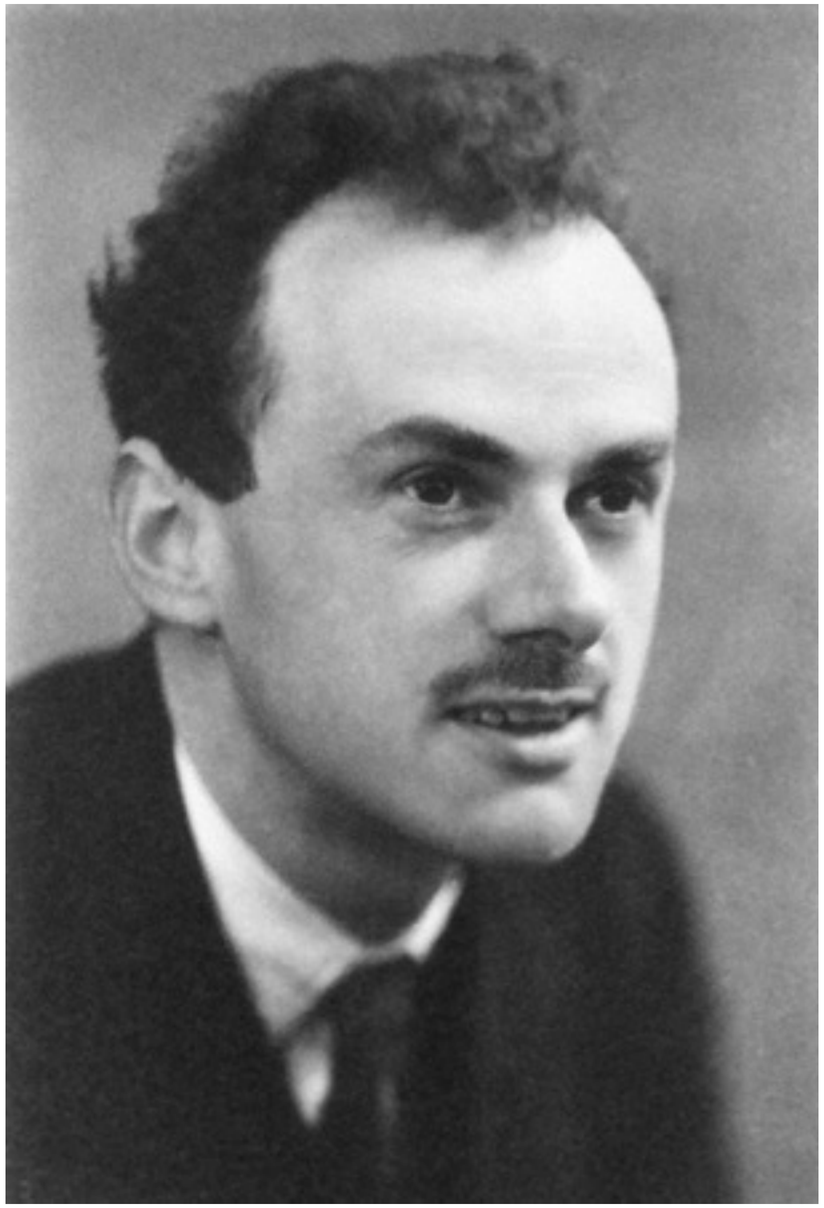
It would be nice to know what wavelengths
a given molecule absorbs

Instead of an experiment in the lab,
I use computational techniques based off of
time-dependent density functional theory



“The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.”

— P.A.M. Dirac

For a given molecule,
try and solve

$$-i\frac{\partial}{\partial t}\Psi = \hat{H}\Psi$$

$$\hat{H}$$

the Hamiltonian describes
interactions between electrons, light, etc.

$$\Psi$$

the wavefunction describes the molecule

$$-i\frac{\partial}{\partial t}$$

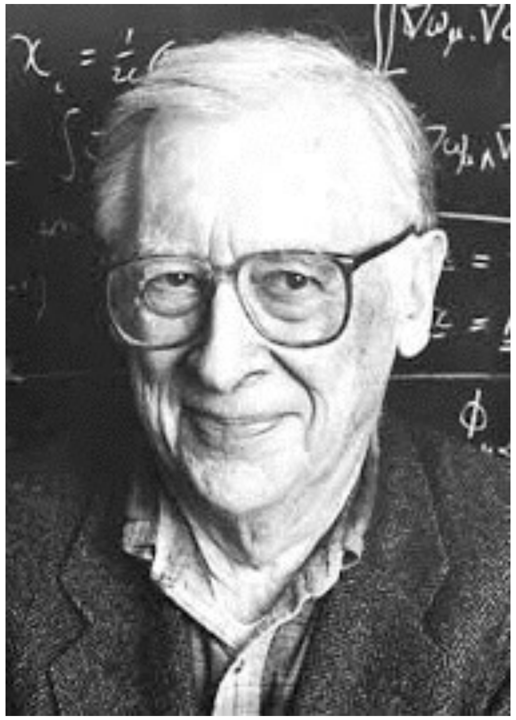
is the time evolution of the system

This is the **Schrodinger Equation**
(and is in general impossible to solve)

In 1998, the Nobel Prize in Chemistry

Kohn

"for his development of
the density-functional theory"



Pople

"for his development of
computational methods in
quantum chemistry"

My research uses the
computational techniques they developed
to understand **how molecules interact with light**

Here’s why the technique is advantageous:

2,3-(S,S)-dimethyloxirane

Let’s say you draw a new molecule;
how do you know what its absorption spectra looks like?

Experimentally:

1. Plan a synthesis

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2. Purchase material

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2. Purchase material
3. Synthesize it

Experimentally:

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2. Purchase material
3. Synthesize it
4. Purify it

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6. Obtain spectra
7. Interpret spectra

Computationally:

1. Input molecule on computer

Computationally:

1. Input molecule on computer
2. Choose a few parameters

Computationally:

1. Input molecule on computer
2. Choose a few parameters
3. Run program

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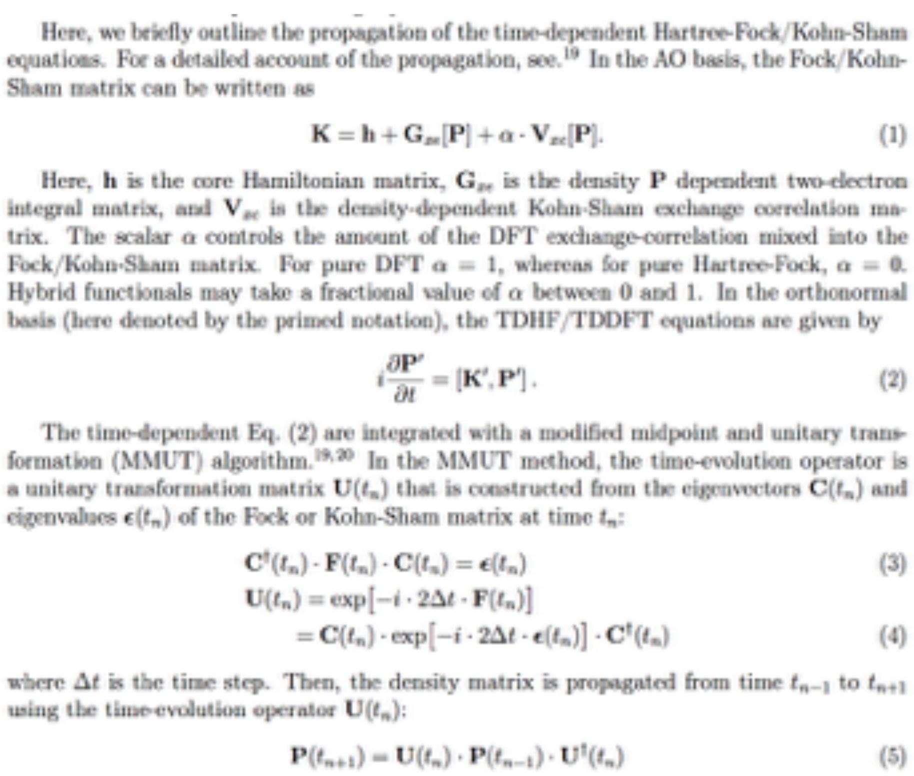
4. Go do something fun

Computationally:

1. Input molecule on computer
2. Choose a few parameters
3. Run program
4. Go do something fun
5. Read results off computer

Obligatory computational slide.

- Real-time time-dependent density functional theory (**RT-TDDFT**)
- No experimental input
- Discretize quantum mechanical equations and implement them on a computer
- Unique because we solve in time
- Allows us to predict molecular properties involving electron dynamics (e.g. spectroscopy, photochemistry, etc.)



Here, we briefly outline the propagation of the time-dependent Hartree-Fock/Kohn-Sham equations. For a detailed account of the propagation, see.[19] In the AO basis, the Fock/Kohn-Sham matrix can be written as

$$\mathbf{K} = \mathbf{h} + \mathbf{G}_{ee}[\mathbf{P}] + \alpha \cdot \mathbf{V}_{xc}[\mathbf{P}]. \tag{1}$$

Here, $\mathbf{h}$ is the core Hamiltonian matrix, $\mathbf{G}_{ee}$ is the density $\mathbf{P}$ dependent two-electron integral matrix, and $\mathbf{V}_{xc}$ is the density-dependent Kohn-Sham exchange correlation matrix. The scalar α controls the amount of the DFT exchange-correlation mixed into the Fock/Kohn-Sham matrix. For pure DFT $\alpha = 1$, whereas for pure Hartree-Fock, $\alpha = 0$. Hybrid functionals may take a fractional value of α between 0 and 1. In the orthonormal basis (here denoted by the primed notation), the TDHF/TDDFT equations are given by

$$i\frac{\partial \mathbf{P}'}{\partial t} = [\mathbf{K}', \mathbf{P}']\,. \tag{2}$$

The time-dependent Eq. (2) are integrated with a modified midpoint and unitary transformation (MMUT) algorithm.[19,20] In the MMUT method, the time-evolution operator is a unitary transformation matrix $\mathbf{U}(t_n)$ that is constructed from the eigenvectors $\mathbf{C}(t_n)$ and eigenvalues $\boldsymbol{\epsilon}(t_n)$ of the Fock or Kohn-Sham matrix at time t_n:

$$\mathbf{C}^{\dagger}(t_n) \cdot \mathbf{F}(t_n) \cdot \mathbf{C}(t_n) = \boldsymbol{\epsilon}(t_n) \tag{3}$$

$$\begin{aligned} \mathbf{U}(t_n) &= \exp\left[-i \cdot 2\Delta t \cdot \mathbf{F}(t_n)\right] \\ &= \mathbf{C}(t_n) \cdot \exp\left[-i \cdot 2\Delta t \cdot \boldsymbol{\epsilon}(t_n)\right] \cdot \mathbf{C}^{\dagger}(t_n) \end{aligned} \tag{4}$$

where Δt is the time step. Then, the density matrix is propagated from time t_{n-1} to t_{n+1} using the time-evolution operator $\mathbf{U}(t_n)$:

$$\mathbf{P}(t_{n+1}) = \mathbf{U}(t_n) \cdot \mathbf{P}(t_{n-1}) \cdot \mathbf{U}^{\dagger}(t_n) \tag{5}$$

So, how is it done?

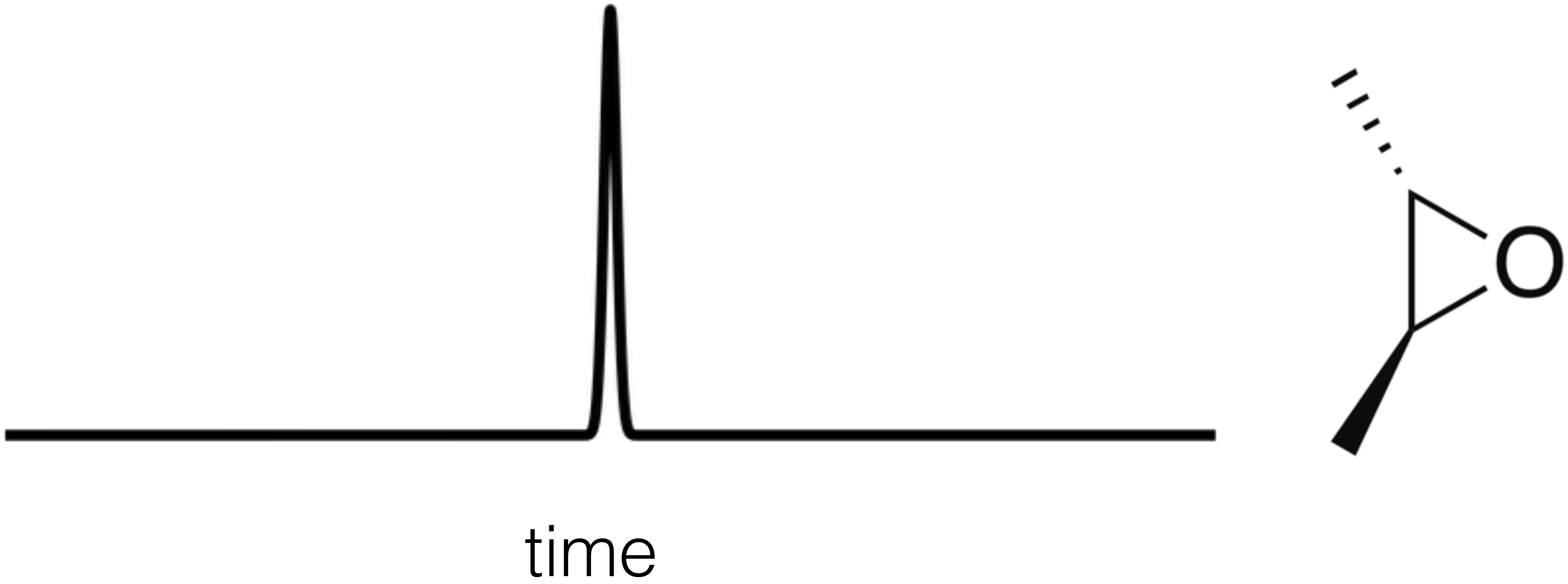
2,3-(S,S)-dimethyloxirane

Experimentally, we sweep over some frequency range

2,3-(S,S)-dimethyloxirane

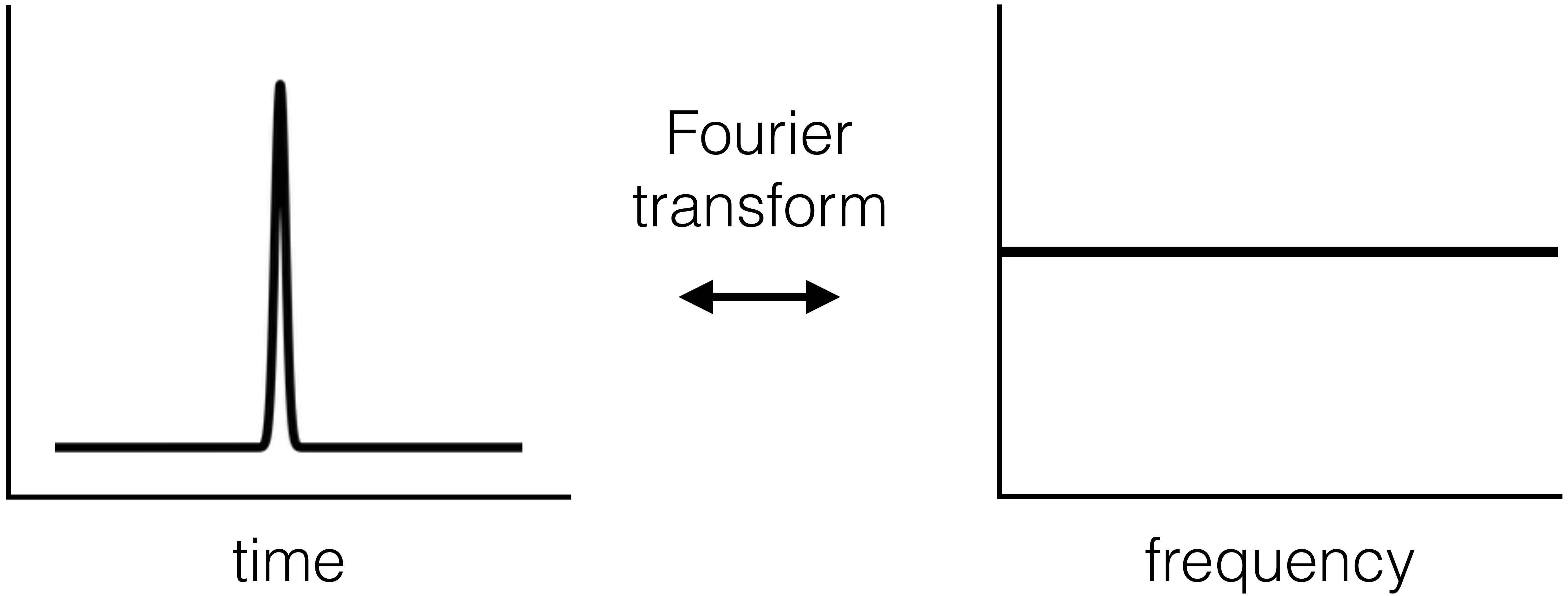
Computationally, we do something similar

We have bit more freedom in choosing our “light source”



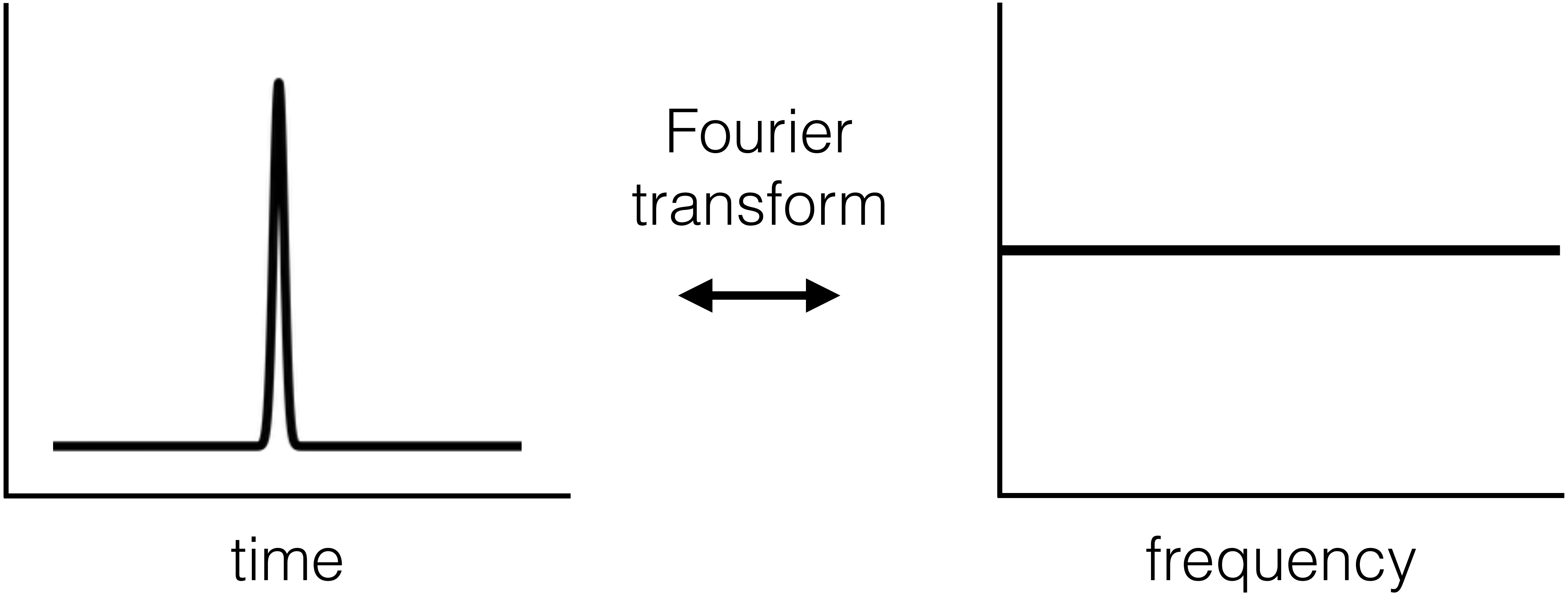
To excite all frequencies, we shoot an infinitely narrow pulse of light at the molecule

To excite all frequencies, we shoot an infinitely narrow pulse of light at the molecule



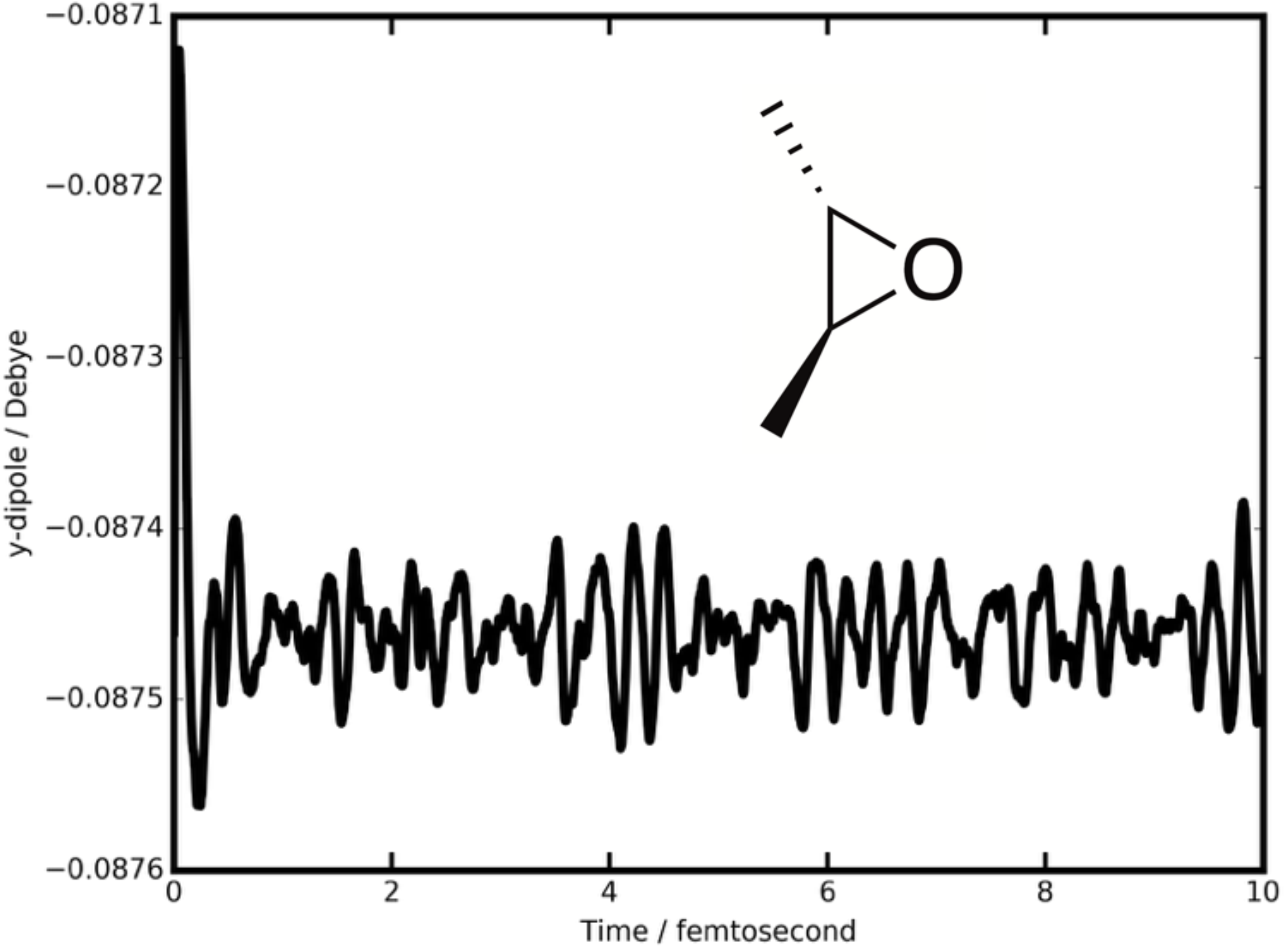
Absorption energies are not in time,
they are in frequency (energy)

This type of pulse is called a delta pulse



This is the Uncertainty Principle in action.

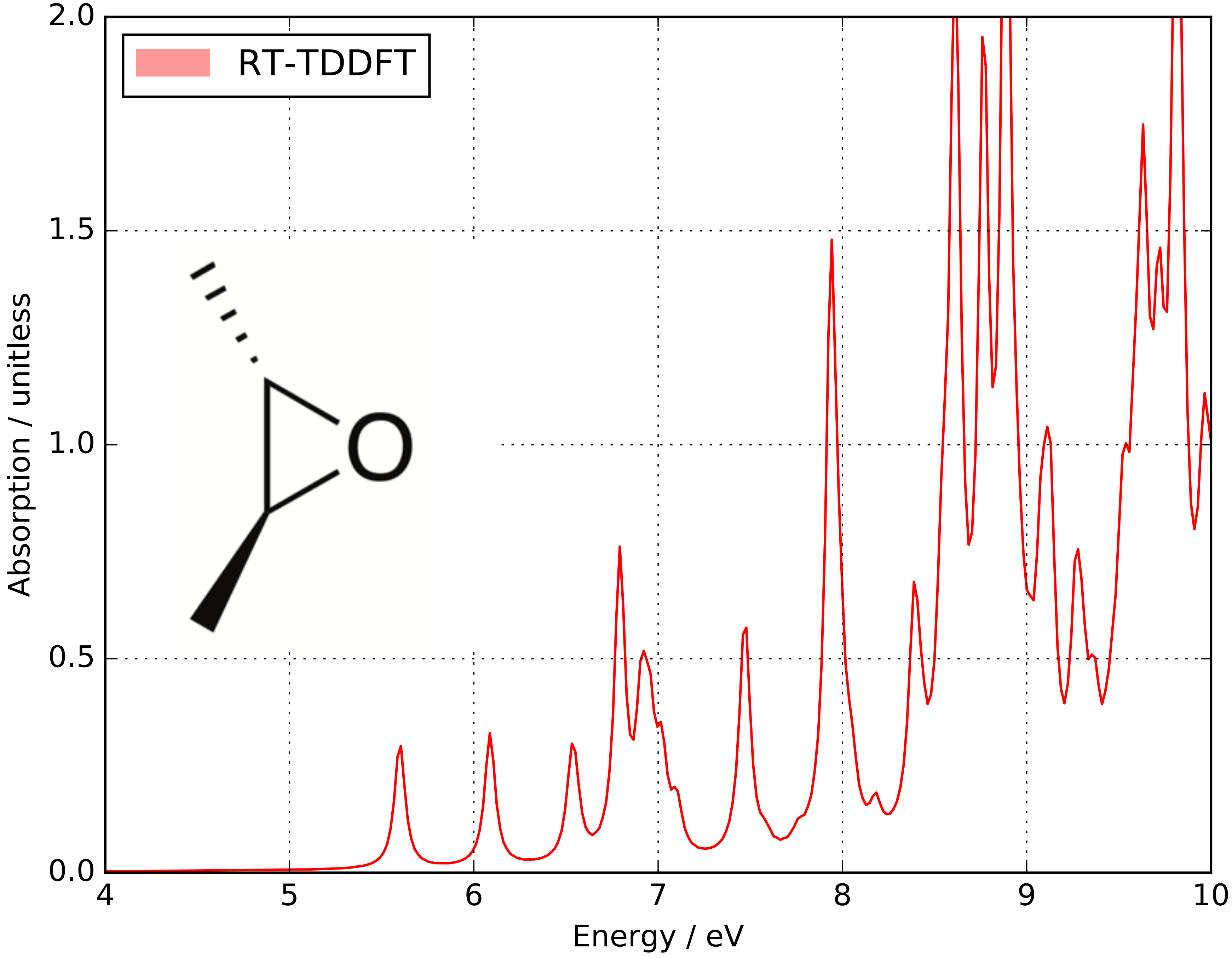
Once we apply the “kick”, we observe the oscillating dipole



$\mu(t)$

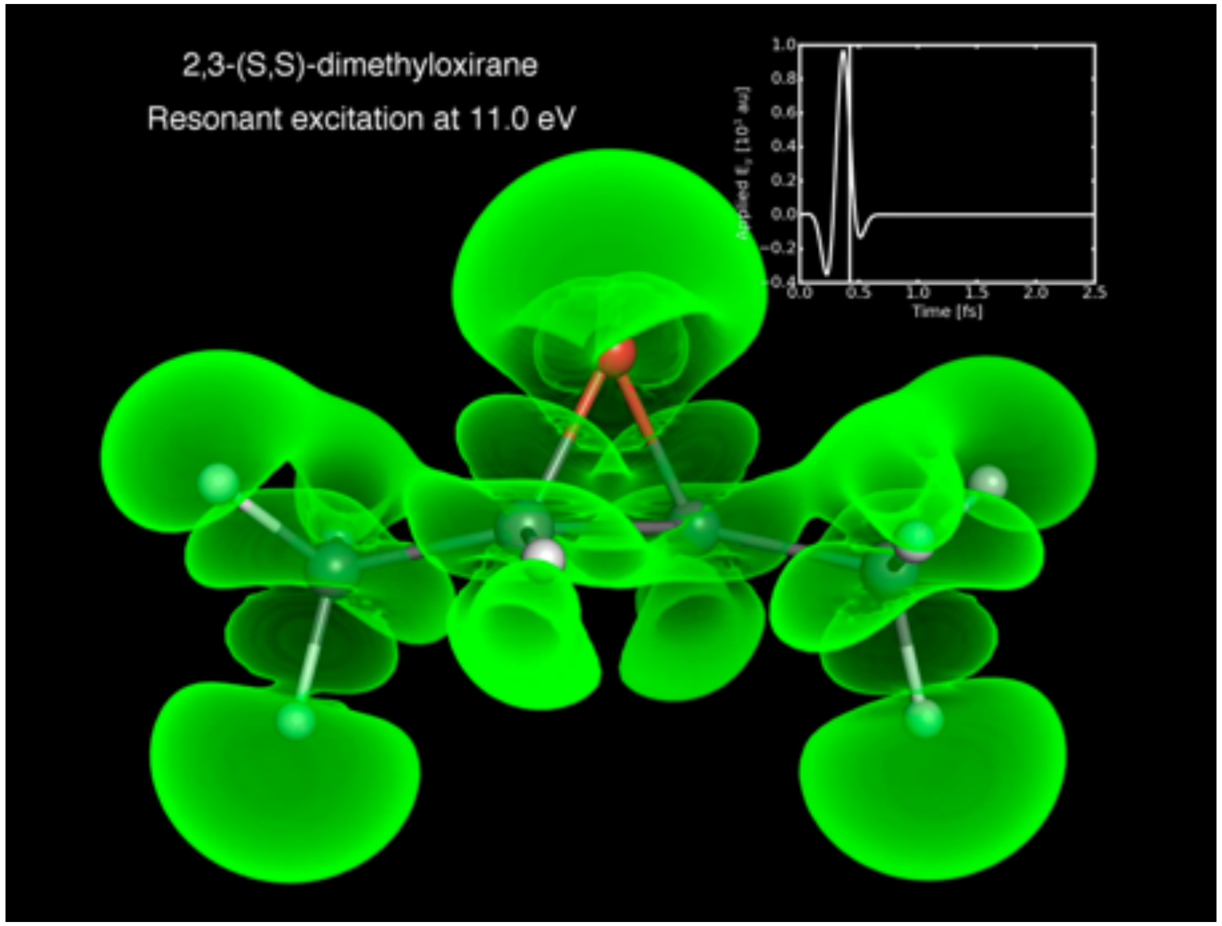
Fourier-transforming the dipole gives us an absorption spectra

$$\frac{4\pi\omega}{3c\kappa}\mathrm{Im}\left[\mathrm{Tr}\left(\mu(\omega)\right)\right]$$



*RT-TDDFT = real-time time-dependent density functional theory

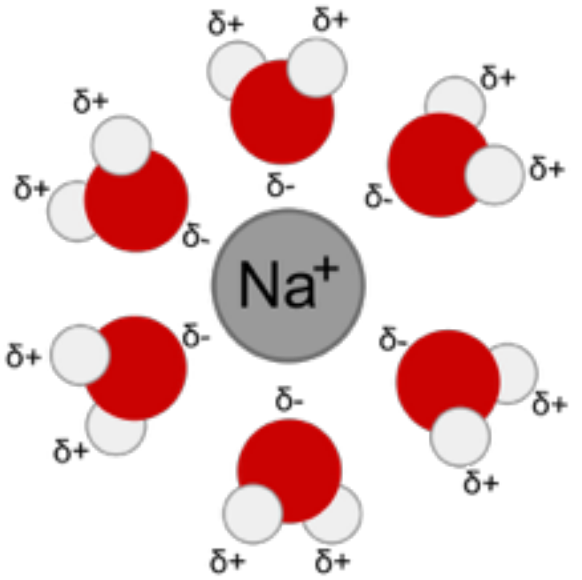
Real-time electronic dynamics gives insight into nature of electronic spectra



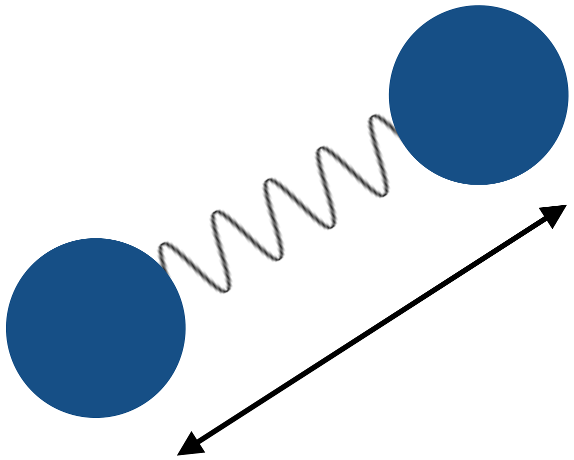
https://youtu.be/blkFqk-GmcY

Of course, the situation is a bit more complicated…

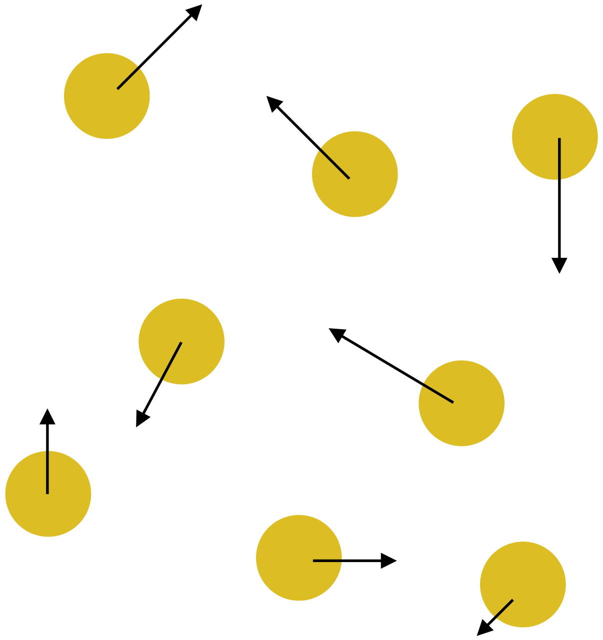
Solvent effects



Nuclei move



Electronic correlation

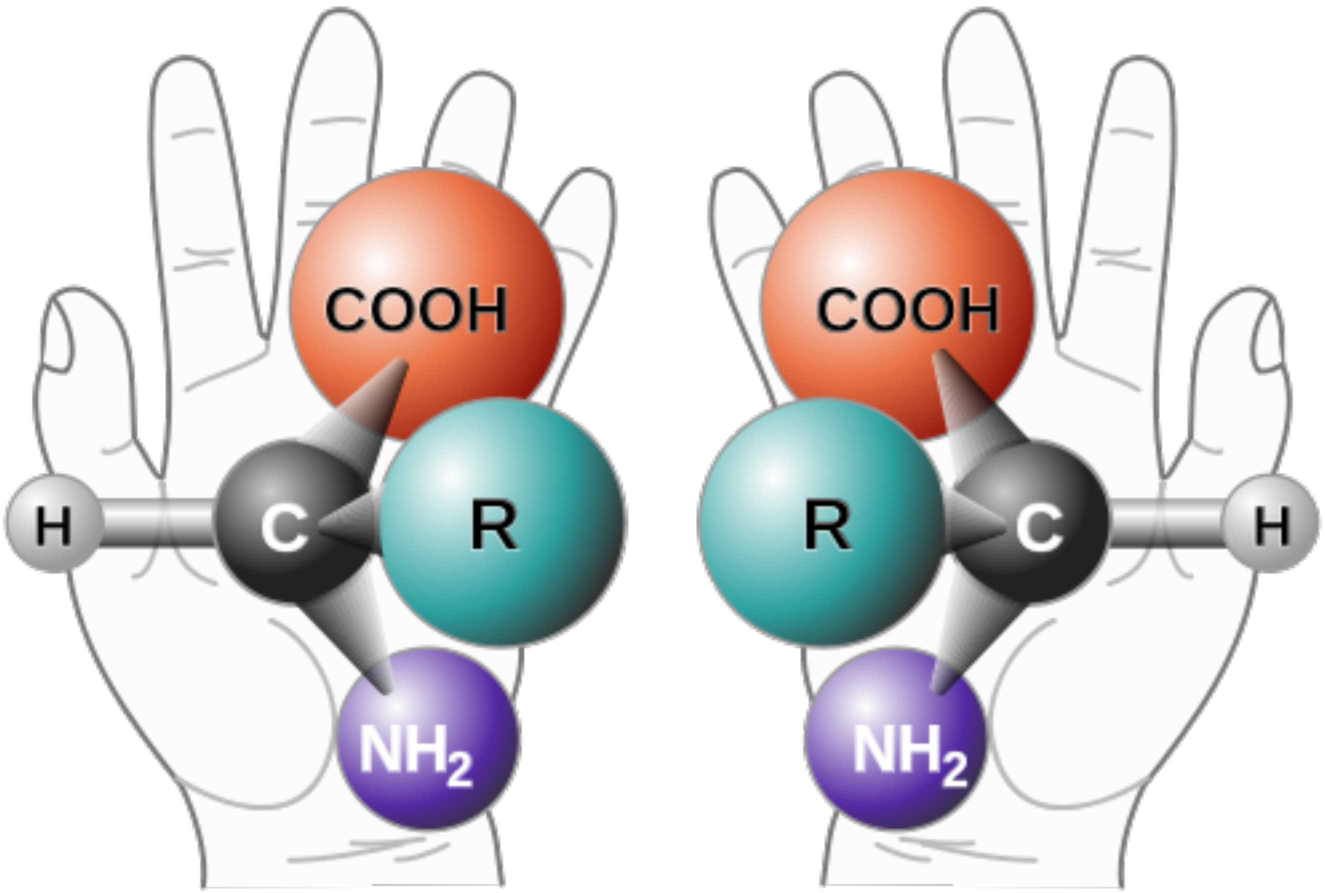


Absorption spectra is just one application

Recently I have applied the real time electron dynamics techniques to computing circular dichroism spectra

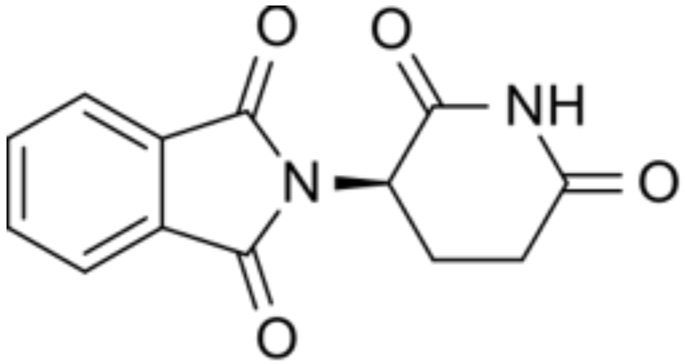
Natural circular dichroism

Differential absorption of circularly polarized light by chiral molecules

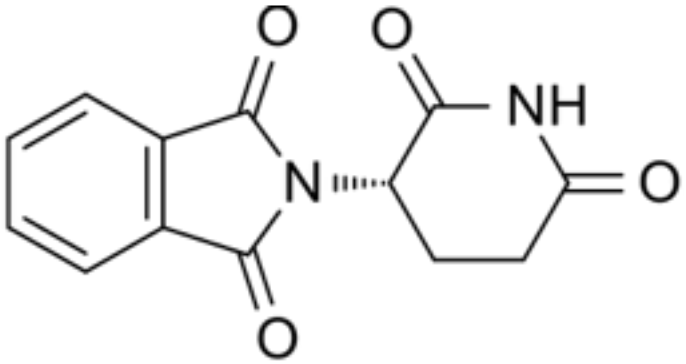


Source: NASA (http://www.nai.arc.nasa.gov/)

Thalidomide tragedy



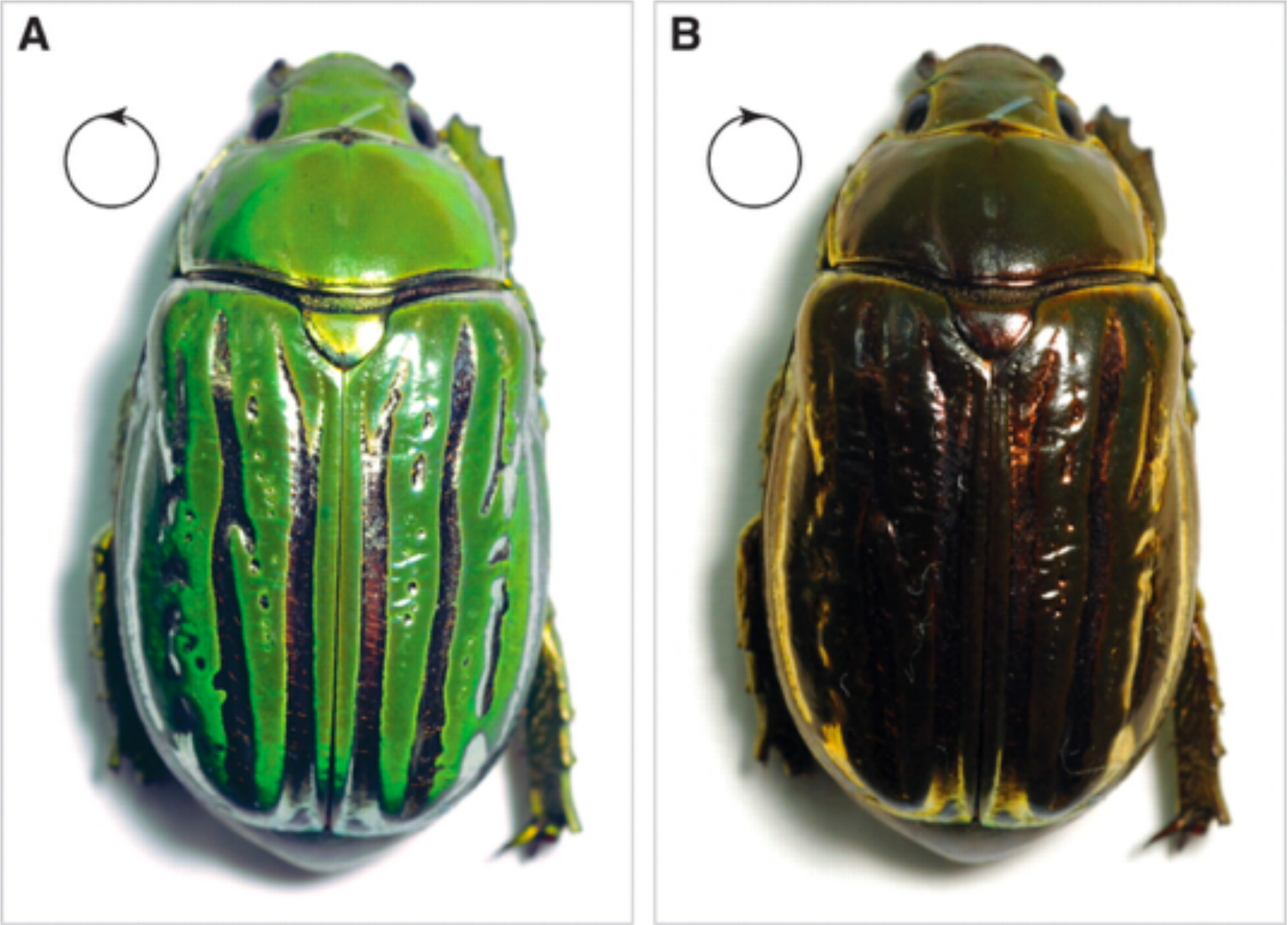
(R)-thalidomide



(S)-thalidomide

Source: Otis Historical Archives National Museum of Health and Medicine

Iridescence of the scarab beetle



Left CP

Right CP

Sharma, Vivek, et al. "Structural origin of circularly polarized iridescence in jeweled beetles." Science 325.5939 (2009): 449-451.

In CD spectroscopy,
we usually care about rotatory strength

$$R(n \leftarrow 0) = \mathrm{Im}\langle 0|\boldsymbol{\mu}|n\rangle\langle n|\boldsymbol{m}|0\rangle$$

Chiral molecules show circular dichroism because the electric field induces a magnetic response

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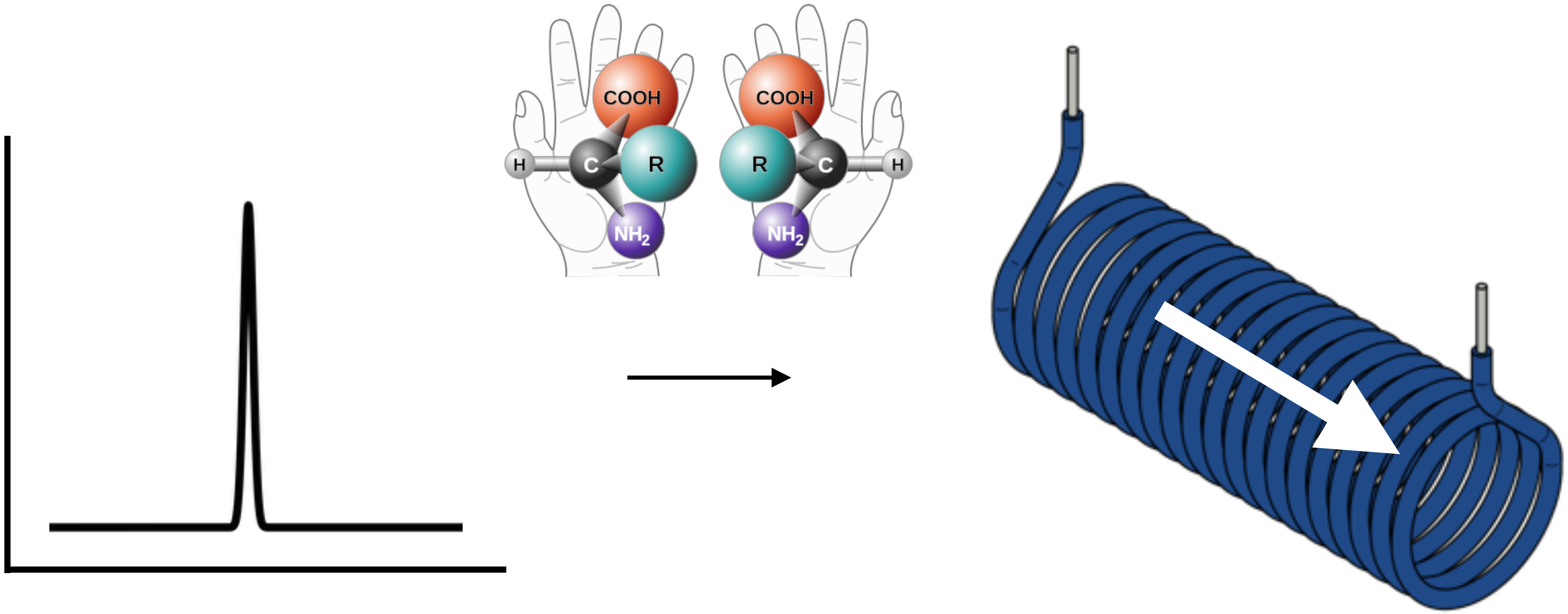
$\boldsymbol{\mu}$	electric dipole
$\boldsymbol{m}$	magnetic dipole

Chiral molecules let electrons “swirl” around

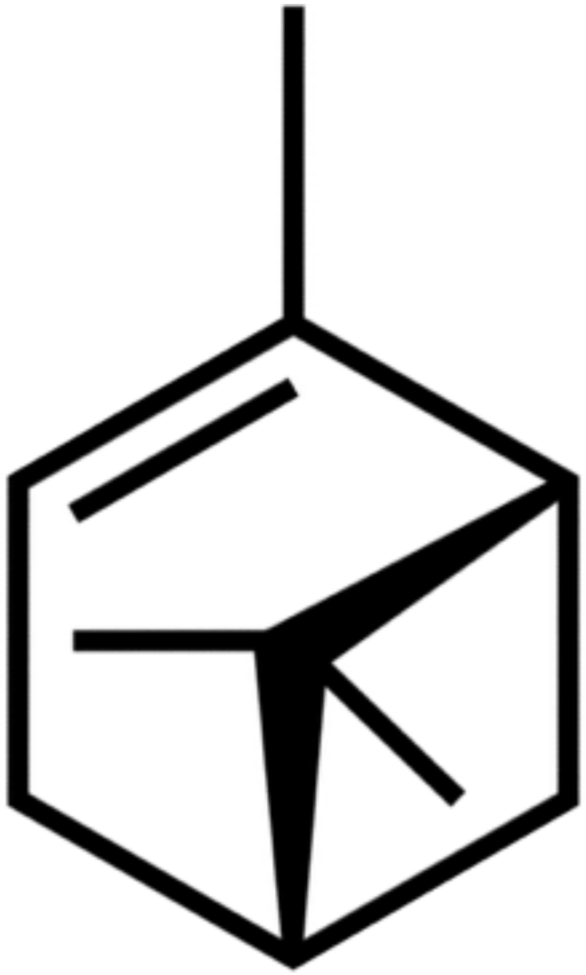


electric field

magnetic dipole

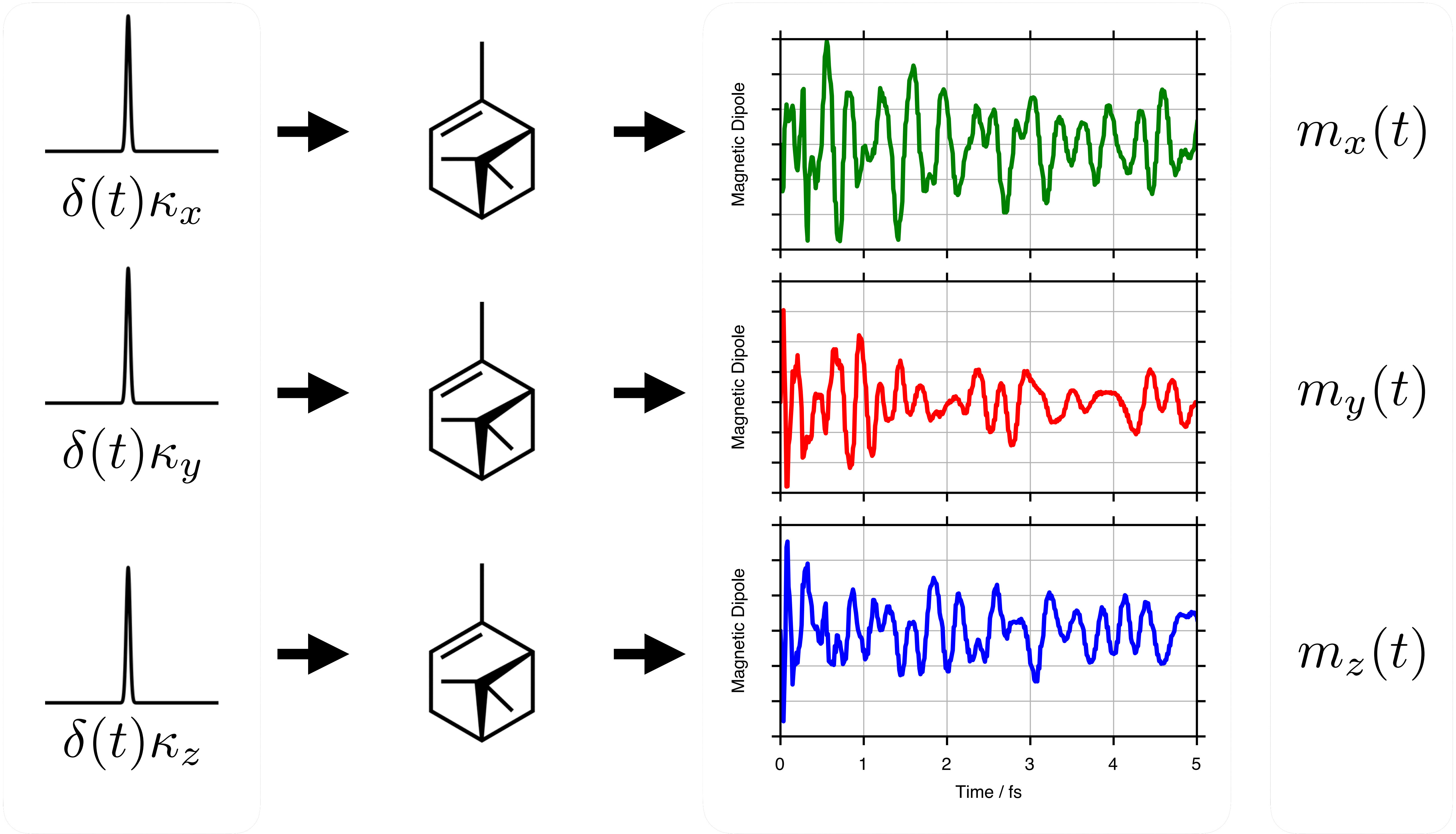
Chiral molecules act like tiny electromagnets

Example: RT-ECD with alpha-1,3-(R,R)-pinene



Perturb with delta $E(t)$

Measure $\boldsymbol{m}(t)$



$\delta(t)\kappa_x$

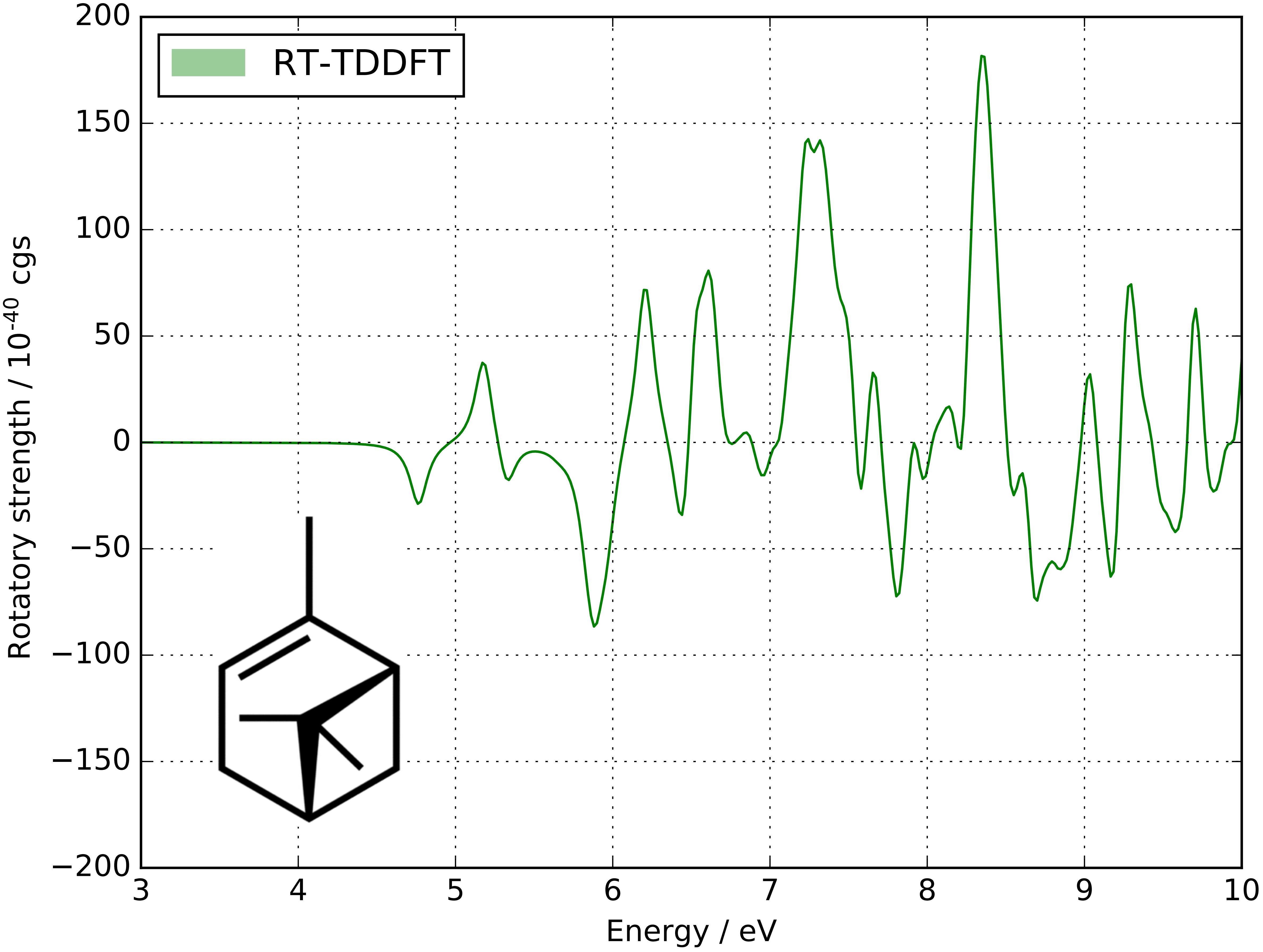
$\delta(t)\kappa_y$

$\delta(t)\kappa_z$

$m_x(t)$

$m_y(t)$

$m_z(t)$



RT-TDDFT = real-time time-dependent density functional theory

If you are feeling particularly brave,
you can try this out for yourself!

Real Time Electronic Dynamics in ChronusQ

https://github.com/liresearchgroup/chronusq_public

Real Time Electronic Dynamics

1. Free & open source!
2. Various types of fields
3. C++/Python

We need beta testers!

In summary:

Real-time time-dependent density functional theory allows us to predict properties of molecules (spectra, color, reactivity) without needing to do an experiment.

Useful for designing molecules and confirming tricky experimental data.

Thank you!