

Vibrational Analysis and Spectroscopy

WP 8 Molecular Dynamics of Time-dependent Phenomena

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Motivation

- Molecules oscillate around equilibrium geometry
- Vibrations can be excited upon irradiation at proper wavelength
- Vibrational spectroscopy (IR, Raman) can be used for characterization and structure elucidation of compounds
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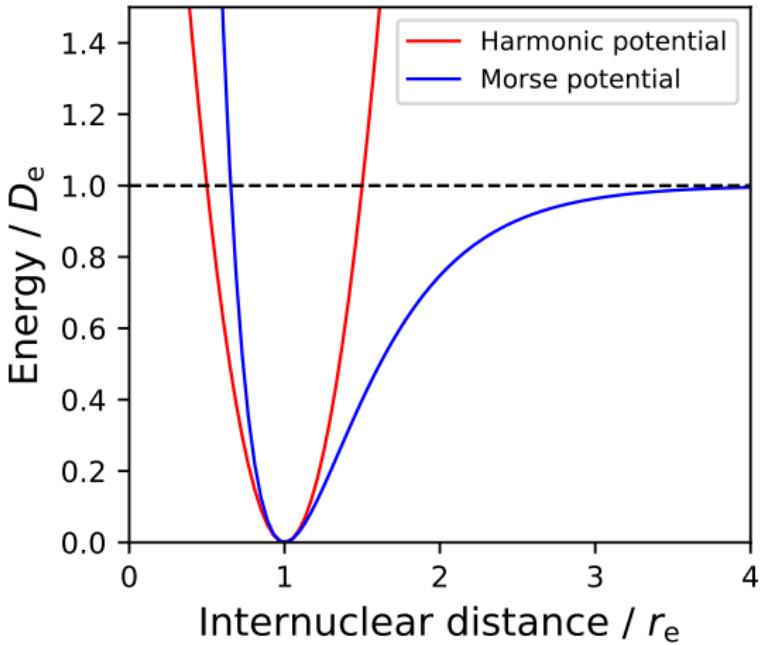
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How?

Potential energy surface (PES)

- We need to evaluate certain properties as functions of the nuclear coordinates
- Accurate modelling of the PES required
- Easiest model: 1D evaluation



PES modelling

① Static approach (QM)

- Solve stationary Schrödinger equation
- + High accuracy (WFT, DFT)
- + Fast
- Small region around (global) minimum geometry is modelled

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② Dynamic approach (MD)

- Model time-dependent evolution of a system
- Nuclear coordinates change, energy is evaluated along the trajectory
- + Better sampling of the PES
- + Good for liquid systems and solvation
- Often less accurate
- Computationally demanding

Born–Oppenheimer approximation

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$$\begin{aligned}\hat{H} &= \hat{T}_e + \hat{T}_N + \hat{V}_{eN} + \hat{V}_{ee} + \hat{V}_{NN} \\ \hat{H} &= -\sum_i^n \frac{1}{2} \vec{\nabla}_i^2 - \sum_I^N \frac{1}{2M_i} - \sum_i^n \sum_I^N \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} \\ &\quad + \sum_i^{n-1} \sum_{j=i+1}^n \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_I^{N-1} \sum_{J=I+1}^N \frac{Z_I Z_J}{|\mathbf{R}_i - \mathbf{R}_J|}\end{aligned}$$

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and assume electrons to instantaneously adjust to the nuclear movement. Hence, we assume $\hat{T}_N = 0$ and $\hat{V}_{NN} = \text{const.}$, ending up at the electronic Hamiltonian \hat{H}_{el}

$$\hat{H}_{el} = \hat{T}_e + \hat{V}_{eN} + \hat{V}_{ee} .$$

Schrödinger equation

Using the electronic Hamiltonian, the electronic Schrödinger equation

$$\hat{H}_{\text{el}}(\mathbf{r}, \mathbf{R})\Psi_{\text{el}}(\mathbf{r}, \mathbf{R}) = E_{\text{el}}(\mathbf{R})\Psi_{\text{el}}(\mathbf{r}, \mathbf{R})$$

can be formulated. It depends *explicitly* on the electronic coordinates but *parametrically* on the nuclear coordinates.

This problem is well known and can be solved for a given nuclear configuration (solving a stationary problem). Sampling of the PES in increments of $\Delta \mathbf{R}$ requires a lot of QM calculations.

⇒ too expensive!

Nuclear Schrödinger equation I

We reinsert the kinetic energy of the nuclei and obtain the nuclear Schrödinger equation:

$$(\hat{T}_N + E_{el})\Psi = E\Psi .$$

When recalling that the nuclei oscillate around the equilibrium geometry R_0 , E_{el} is calculated only once. In the close vicinity it is approximated by a Taylor expansion of E_{el} , which is truncated after the second term:

$$V(\mathbf{R}) = E_{el}(\mathbf{R}_0) + \left(\frac{dE_{el}}{d\mathbf{R}} \right)^T (\mathbf{R} - \mathbf{R}_0) + \frac{1}{2} (\mathbf{R} - \mathbf{R}_0)^T \left(\frac{d^2E_{el}}{d^2\mathbf{R}} \right) (\mathbf{R} - \mathbf{R}_0) .$$

The terms $\left(\frac{d^nE_{el}}{d^n\mathbf{R}} \right)$ are $3N \times 3N$ matrices. $E_{el}(\mathbf{R}_0)$ is chosen as reference energy and therefore, vanishes. \mathbf{R}_0 is a stationary point, hence $\left(\frac{dE_{el}}{d\mathbf{R}} \right) = 0$. We define $\Delta\mathbf{R} = \mathbf{R} - \mathbf{R}_0$ and the second derivatives as force constant matrix \mathbf{F} .

Nuclear Schrödinger equation II

The above expression simplifies to

$$\left(-\sum_i^{3N} \frac{1}{2M_i} \frac{\partial^2}{\partial R_i^2} + \frac{1}{2} \Delta \mathbf{R}^T \mathbf{F} \Delta \mathbf{R} \right) \Psi = E \Psi ,$$

which is well known as the harmonic oscillator. For the one-dimensional case, this expression can be written as

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which is well known as the harmonic oscillator. For the one-dimensional case, this expression can be written as

$$\left(-\frac{1}{2\mu} \frac{d}{dx} + \frac{1}{2} kx^2 \right) \Psi = E \Psi .$$

Next, mass-weighted coordinates \mathbf{y} are introduced as

$$y_i = \sqrt{M_i} \Delta R_i , \quad \frac{\partial^2}{\partial y_i^2} = \frac{1}{M_i} \frac{\partial^2}{\partial R_i^2} .$$

Mass-weighted nuclear Schrödinger equation

Along with this, the force constant matrix \mathbf{F} is also transformed into a mass-weighted form \mathbf{F}'

$$F'_{ij} = \frac{F_{ij}}{\sqrt{M_i M_j}},$$

yielding a nuclear Schrödinger equation of the form

$$\left(-\sum_i^{3N} \frac{1}{2} \frac{\partial^2}{\partial y_i^2} + \frac{1}{2} \mathbf{y}^T \mathbf{F}' \mathbf{y} \right) \Psi = E \Psi.$$

This is a $3N$ -dimensional problem because the dimensions are coupled via \mathbf{F} . To uncouple the differential equations, \mathbf{F} must be diagonalized (removing all off-diagonal elements). The diagonalization is achieved by a unitary transformation which corresponds to a rotation of the coordinate system.

Unitary transformation

With the unitary matrix \mathbf{U} , the coordinates are transformed:

$$\mathbf{q} = \mathbf{Uy} ,$$

which leads to a reformulated nuclear Schrödinger equation:

$$\left(-\sum_i^{3N} \frac{1}{2} \frac{\partial^2}{\partial q_i^2} + \frac{1}{2} \mathbf{q}^T \mathbf{U} \mathbf{F}' \mathbf{U}^T \mathbf{q} \right) \Psi = E\Psi .$$

The diagonalized force constant matrix $\mathbf{U}\mathbf{F}'\mathbf{U}$ is termed Hessian matrix \mathbf{H} , not to be confused with the Hamiltonian \hat{H} :

$$\left(-\sum_i^{3N} \frac{1}{2} \frac{\partial^2}{\partial q_i^2} + \frac{1}{2} \mathbf{q}^T \mathbf{H} \mathbf{q} \right) \Psi = E\Psi .$$

Separation into one-dimensional problems

As the Hessian \mathbf{H} is diagonal in the transformed coordinate system, the vectors \mathbf{q} are the eigenvectors of \mathbf{H} ,

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$$\mathbf{H} \mathbf{q}_i = \lambda_i \mathbf{q}_i .$$

Inserting this into the nuclear Schrödinger equation, we end up at

$$-\sum_i^{3N} \left(\frac{1}{2} \frac{\partial^2}{\partial q_i^2} + \frac{1}{2} \lambda_i q_i^2 \right) \Psi = E \Psi .$$

This is analogue to $3N$ uncoupled one-dimensional harmonic oscillator problems:

$$\left(-\frac{1}{2\mu} \frac{d}{dx} + \frac{1}{2} kx^2 \right) \Psi = E \Psi .$$

Vibrational frequencies

As a last step, the vibrational frequencies ν_i can be derived analogously to the harmonic oscillator ν_i^{HO}

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$$\nu_i^{HO} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} ,$$
$$\nu_i = \frac{1}{2\pi} \sqrt{\lambda_i} .$$

In practice, five or six eigenvalues of the Hessian are 0

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$$\nu_i^{HO} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} ,$$
$$\nu_i = \frac{1}{2\pi} \sqrt{\lambda_i} .$$

In practice, five or six eigenvalues of the Hessian are 0 because these correspond to the translational and rotational degrees of freedom. Negative eigenvalues proof the stationary geometry to be a saddle point. If all eigenvalues are positive, a true minimum of the PES was found.

Spectroscopic Intensities I

Most QC codes available today rely on the *double harmonic approximation*:

- ① All vibrational modes are assumed as harmonic oscillators
- ② The fundamental properties describing the spectroscopic intensities are determined by the first-order geometric derivative of the polarization property governing the spectroscopic phenomenon under study

→ IR:

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 - IR: molecular electric dipole moment μ
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IR Intensities I

From basic QC, we invoke that the transition rate $W_{k \rightarrow f}$ from an initial state $|k\rangle$ to a final state $|f\rangle$ induced by a perturbation operator \hat{H}' reads

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$$W_{k \rightarrow f} \propto \left| \langle f | \hat{H}' | k \rangle \right|^2 .$$

The system is perturbed by electromagnetic radiation (e.g. IR). The perturbation is approximated as a dipole, meaning

$$\hat{H}' = -\langle e_g | \mu \mathbf{E} | e_g \rangle = -\langle e_g | \mu | e_g \rangle \mathbf{E}_0 = -\mu(\mathbf{q}) \mathbf{E}_0 ,$$

while assuming the electric field \mathbf{E} to be constant over the extent of the molecule. The dipole moment is obtained as a function of the nuclear coordinates $\mu(\mathbf{q})$ by calculating the expectation value with the electronic ground state $|e_g\rangle$.

IR Intensities II

The dipole moment is then expanded in a Taylor series up to first order:

$$\mu(\mathbf{q}) = \mu_0 + \sum_{i=1}^{3N-6} \left(\frac{\partial \mu(\mathbf{q})}{\partial q_i} \right) q_i .$$

When inserting analytical expressions for this term, we end up at the following expression for the absorption coefficients A_i for the vibrational modes i of the fundamental excitation:

$$A_i = \frac{N_A}{12\epsilon_0 c^2} \left(\frac{\partial \mu(\mathbf{q})}{\partial q_i} \right)^2 .$$

This shows, that only those vibrational modes which cause a change of the molecular dipole moment along the mode, show up in the IR spectrum.

Raman Intensities I

For the Raman intensities, a similar approach is used: According to the Placzek classical theory of polarization, the electric field induces a dipole moment μ^{ind} in the molecule and the Intensity I is proportional to

$$I \propto |\langle \mu^{\text{ind}} \rangle|^2 ,$$

$$\langle \mu^{\text{ind}} \rangle = \langle f | \alpha(\mathbf{q}) | k \rangle \mathbf{E}_0 .$$

with the initial and final states $|k\rangle, |f\rangle$ and the assumption of a constant electric field E over the extend of the molecule. The molecular polarizability $\alpha(\mathbf{q})$ is expanded in a Taylor series up to the first order:

$$\alpha(\mathbf{q}) = \alpha_0 + \sum_{i=1}^{3N-6} \left(\frac{\partial \alpha(\mathbf{q})}{\partial q_i} \right) q_i .$$

Raman Intensities II

After inserting analytical expressions for the respective terms, we yield the intensities I_i for the vibrational modes i . In experimental Raman spectroscopy, the scattered intensities can be measured in different directions with respect to the incident beam:

$$I_i^{\parallel} = C \frac{(\tilde{\nu}_{\text{in}} - \tilde{\nu}_i)^4}{\tilde{\nu}_i(1 - \exp\left(-\frac{hc\tilde{\nu}_i}{k_B T}\right))} \left(\frac{\partial \alpha_{xx}(\mathbf{q})}{\partial q_i} \right)^2 ,$$

$$I_i^{\perp} = C \frac{(\tilde{\nu}_{\text{in}} - \tilde{\nu}_i)^4}{\tilde{\nu}_i(1 - \exp\left(-\frac{hc\tilde{\nu}_i}{k_B T}\right))} \left(\frac{\partial \alpha_{xy}(\mathbf{q})}{\partial q_i} \right)^2 .$$

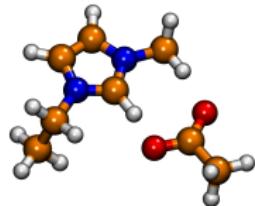
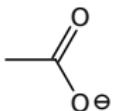
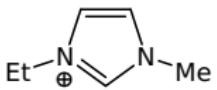
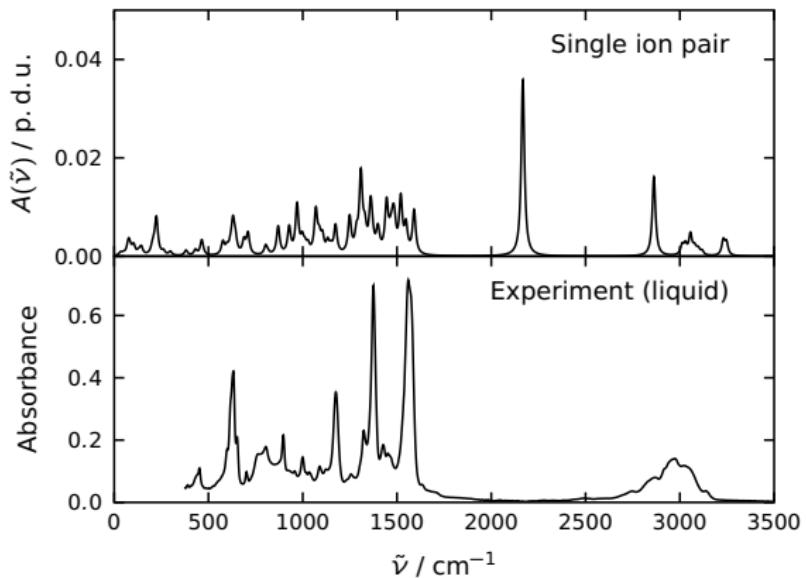
This shows, that only those vibrational modes which cause a change of the molecular polarizability along the mode, show up in the Raman spectrum.

Molecular dynamics

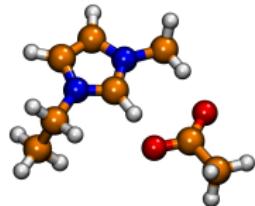
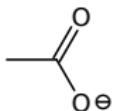
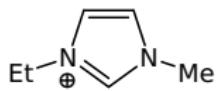
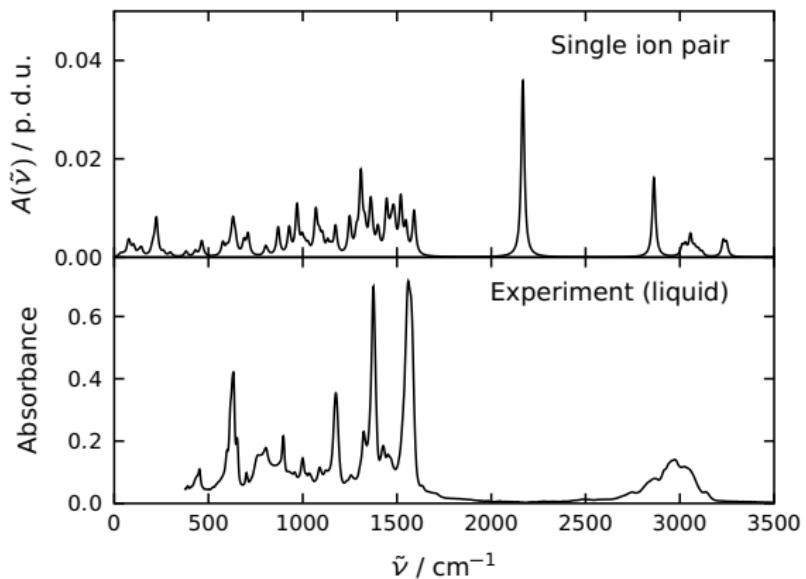
Molecular Dynamics
vs.
Static Quantum Chemistry

What are the differences?

Spectroscopy in the liquid phase

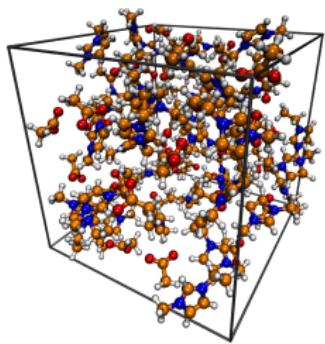
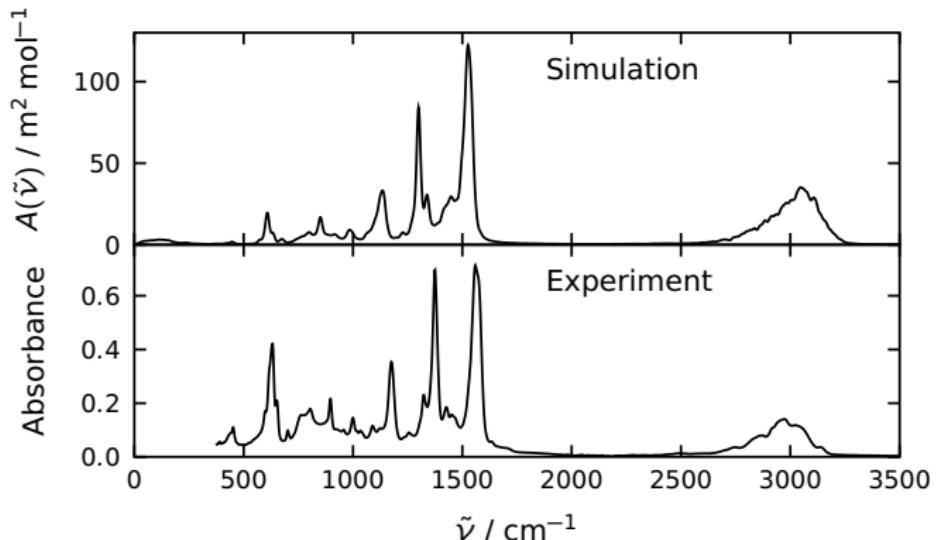


Spectroscopy in the liquid phase



- Carbene formation in the gas phase
- isolated ion pair not sufficient to model the IR spectrum of the liquid phase

Spectroscopy in the liquid phase



- Calculate spectrum from AIMD simulation
- Accounts for explicit solvation effects, polarization, dynamics, anharmonicity and conformational averaging

Green–Kubo approach

- **Green–Kubo:**

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- Express time-dependent phenomena as integrals over correlation-functions

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- **Correlation functions:**

- Take data sets x and y and investigate which correlation exists between them

$$r_{xy} = \frac{\sum(x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum(x_i - \bar{x})^2 \sum(y_i - \bar{y})^2}}$$

- Provides statistical relationship between variables

Wiener–Khintchine theorem

- Relates the Fourier transform of $f(t)$ to the autocorrelation function

Wiener–Khintchine theorem

- Relates the Fourier transform of $f(t)$ to the autocorrelation function
- Autocorrelation function can be calculated by
 - 1. Taking the square of the absolute value of its Fourier transform

$$\langle C(\tau)C(t+\tau) \rangle_\tau = \frac{1}{2\pi} \int \left| \int f(t) e^{-i\omega t} dt \right|^2 e^{i\omega t} d\omega$$

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- 2. Applying the inverse Fourier transform

$$\langle C(\tau)C(t+\tau) \rangle_\tau = \frac{1}{2\pi} \int \left| \int f(t) e^{-i\omega t} dt \right|^2 e^{i\omega t} d\omega$$

- **Advantage:** Fast Fourier transform algorithms are faster than a direct computation of the autocorrelation function

Correlation functions for vibrational spectra

- **Infrared:**

$$A(\tilde{\nu}) \propto \int \langle \dot{\mu}(\tau) \cdot \dot{\mu}(t + \tau) \rangle_{\tau} e^{-2\pi i c \tilde{\nu} t} dt$$

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- **Raman:**

$$I(\tilde{\nu}) \propto \frac{(\tilde{\nu}_{in} - \tilde{\nu})^4}{\tilde{\nu} \left(1 - \exp \left(-\frac{hc\tilde{\nu}}{k_B T} \right) \right)} \\ \times \int (\langle \dot{\alpha}_{xx}(\tau) \dot{\alpha}_{xx}(t + \tau) \rangle + \langle \dot{\alpha}_{xy}(\tau) \dot{\alpha}_{xy}(t + \tau) \rangle) e^{-2\pi i c \tilde{\nu} t} dt$$

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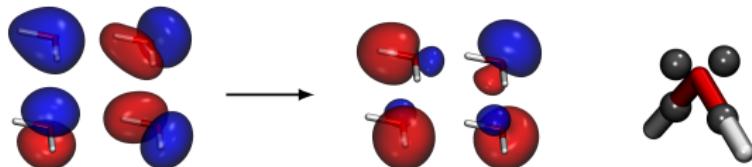
- **Vibrational circular dichroism:**

$$\Delta A(\tilde{\nu}) \propto \int \left[\langle \dot{\mu}(\tau) \cdot \dot{\mathbf{m}}(t + \tau) \rangle_{\tau} - \langle \dot{\mathbf{m}}(\tau) \cdot \dot{\mu}(t + \tau) \rangle_{\tau} \right] e^{-2\pi i c \tilde{\nu} t} dt$$

Wannier functions

Dipole moment

- Established approach: Maximally localized Wannier functions



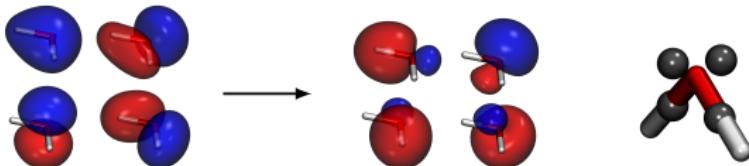
- Wannier function centers as locations of electron pairs
- Dipole moment as sum over point charges

$$\mu = -2e \sum_{i \in \text{Wan.}} \mathbf{r}_i + e \sum_{j \in \text{Nuc.}} Z_j \mathbf{R}_j$$

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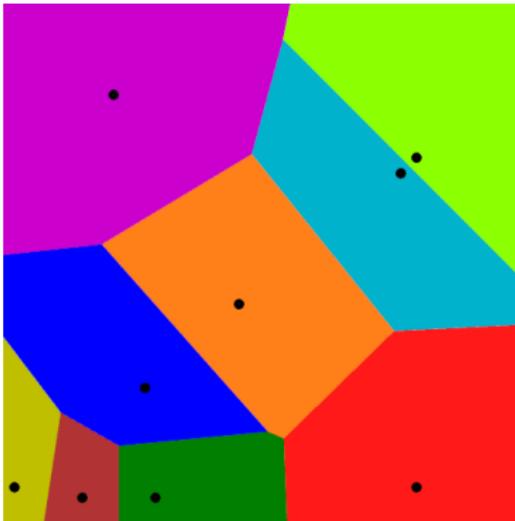
Polarizability

- Recalculate orbitals with external electric field

$$\mu_{\text{ind}} = \alpha \mathbf{E}$$

- Polarizability by finite differences

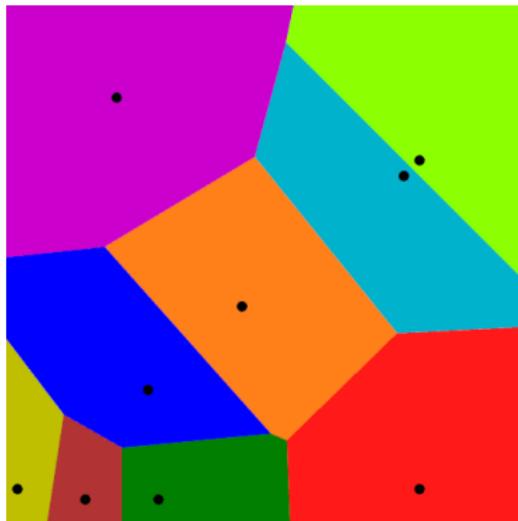
Voronoi tessellation



- Division of Euclidean space into set of Voronoi cells
- Each point in space assigned to a site s_i to which it is closest

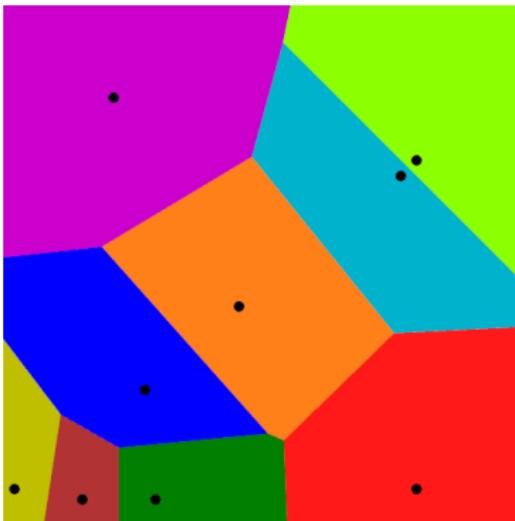
$$C_i = \{\mathbf{x} \in \mathbb{R}^3 \mid (\mathbf{x} - \mathbf{s}_i)^2 \leq (\mathbf{x} - \mathbf{s}_j)^2 \forall j \neq i\}; i, j = 1, \dots, n$$

Voronoi tessellation



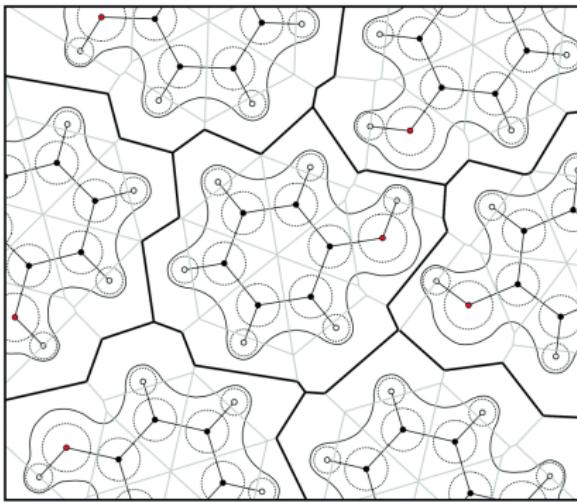
- Traditional Voronoi tessellation can be problematic for molecules

Voronoi tessellation



- Traditional Voronoi tessellation can be problematic for molecules
- Electron density is equally distributed in covalent bonds
 - No electronegativity and bond polarization

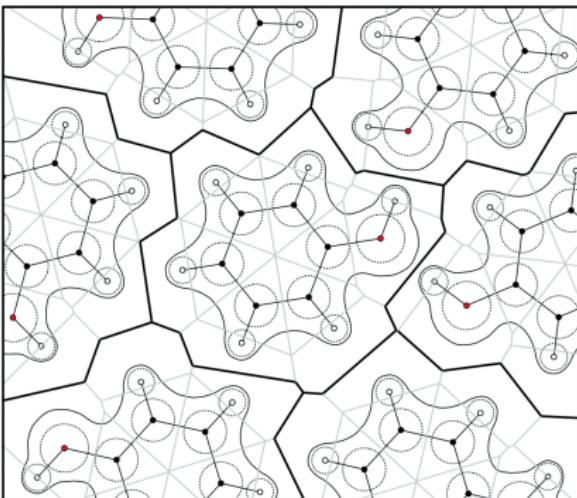
Radical Voronoi tessellation



- radical Voronoi tessellation assigns radii r_i to each site

$$C_i^r = \{\mathbf{x} \in \mathbb{R}^3 \mid (\mathbf{x} - \mathbf{s}_i)^2 - r_i^2 \leq (\mathbf{x} - \mathbf{s}_j)^2 - r_j^2 \forall j \neq i\}; i, j = 1, \dots, n$$

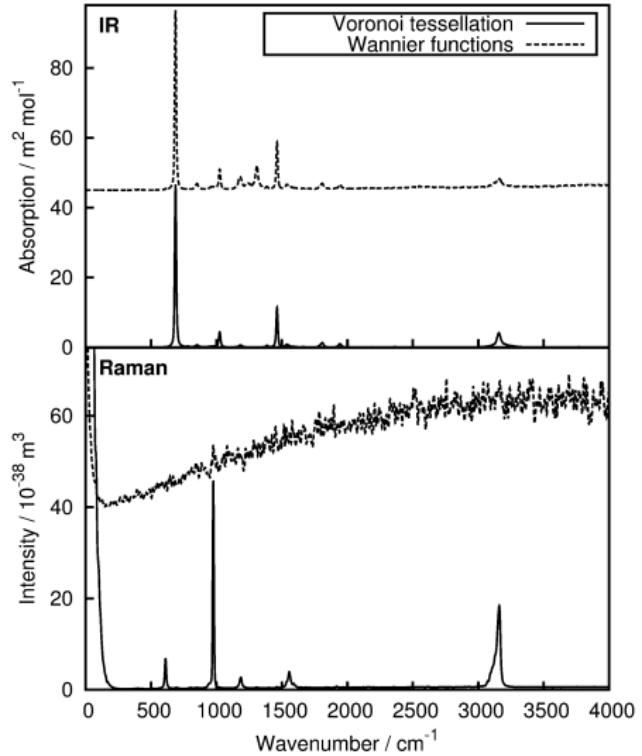
Radical Voronoi tessellation



- merge atomic cells to molecular cells
- integrate electron density in molecular cells to obtain molecular dipole moments

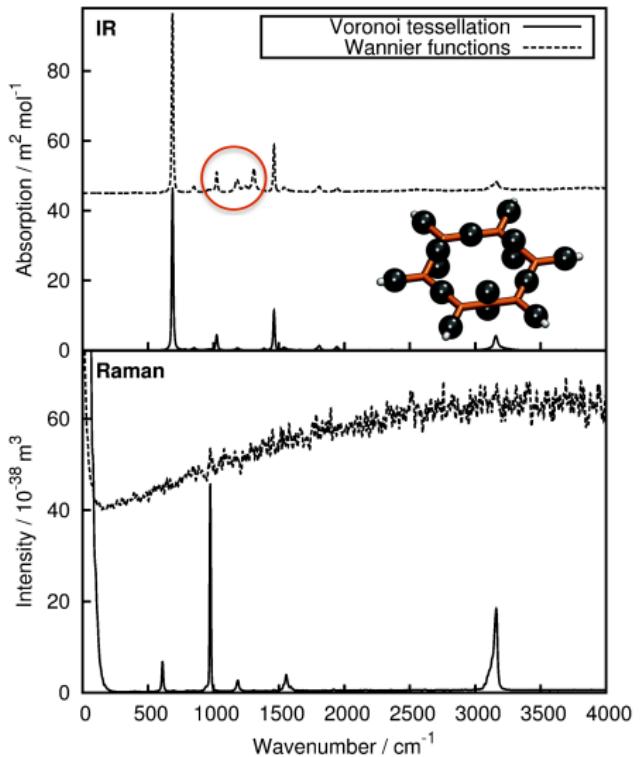
$$\mu_k = \int_{M_k} \mathbf{r} \rho(\mathbf{r}) d\mathbf{r}$$

IR and Raman spectra of benzene

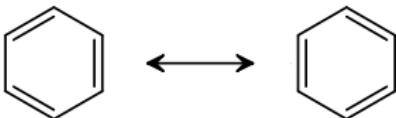


- Compare Voronoi and Wannier, what do you recognize?

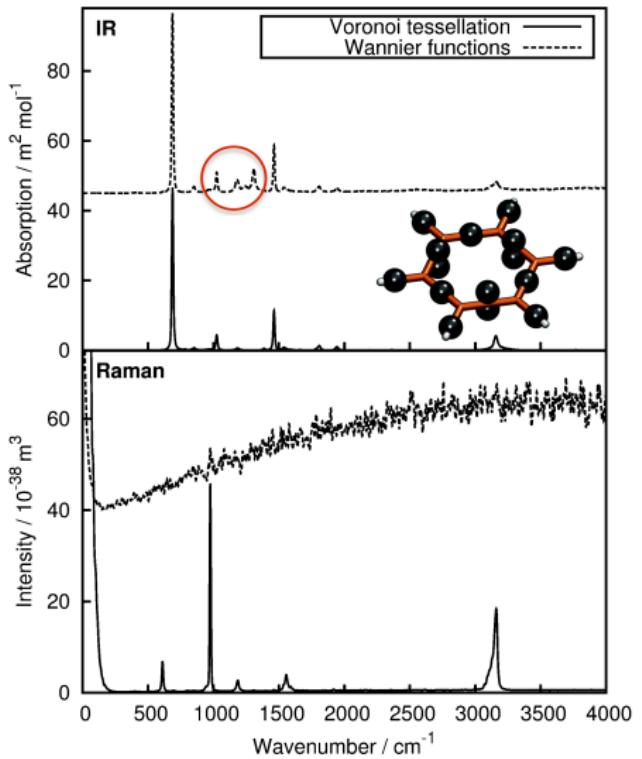
IR and Raman spectra of benzene



- **IR:** Wannier predicts additional bands between 1200 cm⁻¹ and 1350 cm⁻¹
 - symmetry breaking by Wannier functions, localization produces alternating single and double bonds in the ring
 - Wannier function centers are regularly interchanging in the trajectory causing artificial dipole moment changes



IR and Raman spectra of benzene



- **Raman:** Wannier does not produce a useful spectrum
 - polarizabilities are obtained by electronic structure calculations with and without an external electric field
 - localization algorithm does not converge to same bond pattern in the two electronic structure calculations
 - polarizability artificially increased by orders of magnitude

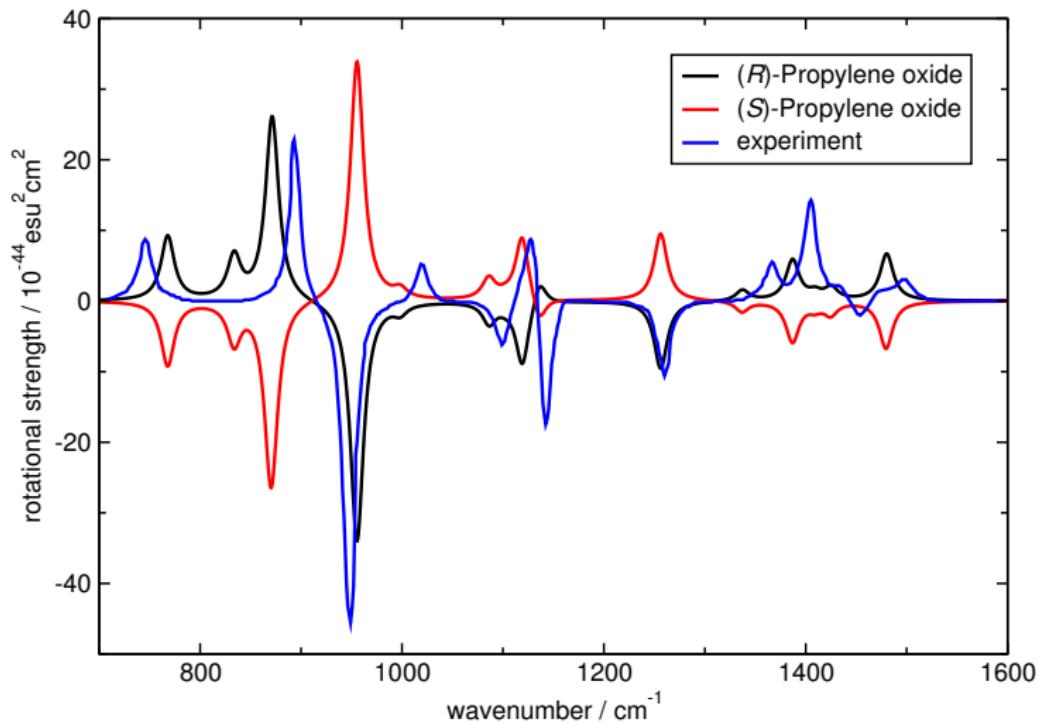
Vibrational circular dichroism

- measures differential absorbance of left- and right-circularly polarized infrared radiation during vibrational transitions

$$\Delta A = A_L - A_R$$

- for chiral molecules ΔA is unequal to zero
- enantiomers show either a positive or negative band for each vibrational mode

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- Correlation function:**

$$\Delta A(\tilde{\nu}) \propto \int \left[\langle \dot{\mu}(\tau) \cdot \dot{\mathbf{m}}(t + \tau) \rangle_{\tau} - \langle \dot{\mathbf{m}}(\tau) \cdot \dot{\mu}(t + \tau) \rangle_{\tau} \right] e^{-2\pi i c \tilde{\nu} t} dt$$

Thomas–Kirchner approach

- classical expression for magnetic dipole moment \mathbf{m}

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- electric current density is product of electron density and scalar field

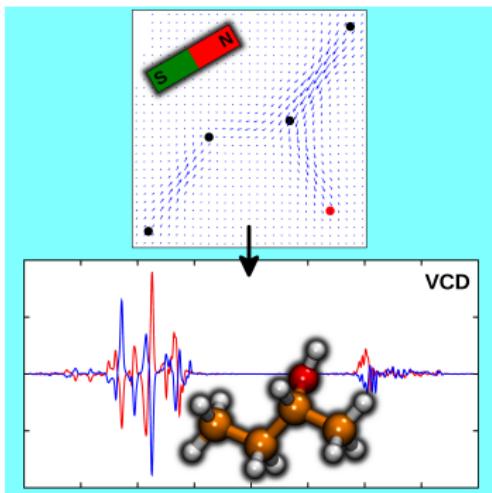
$$\mathbf{j}(\mathbf{r}, t) = -\rho(\mathbf{r}, t) \nabla \alpha(\mathbf{r}, t)$$

Thomas–Kirchner approach

- combining both conditions yields differential equation

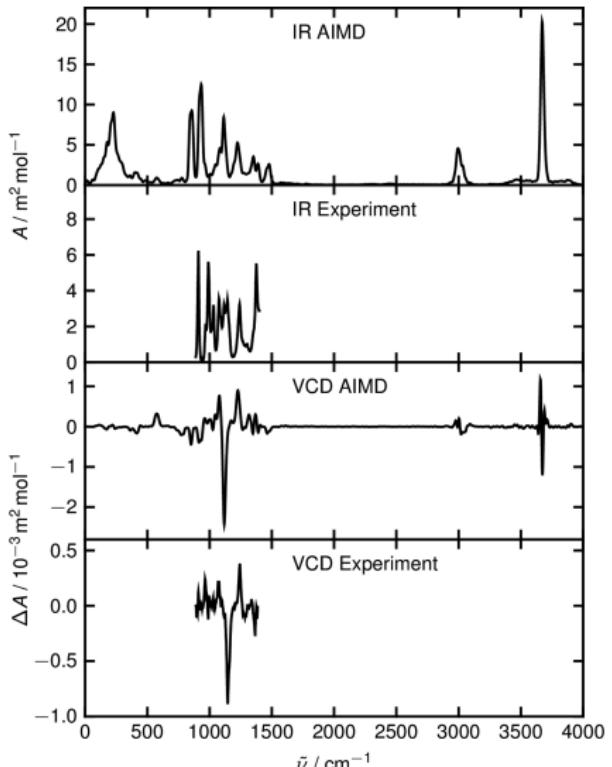
$$\frac{\partial \rho(\mathbf{r}, t)}{\partial t} = \nabla \rho(\mathbf{r}, t) \cdot \nabla \alpha(\mathbf{r}, t) + \rho(\mathbf{r}, t) \Delta \alpha(\mathbf{r}, t)$$

- solve to obtain scalar field $\alpha(\mathbf{r}, t)$

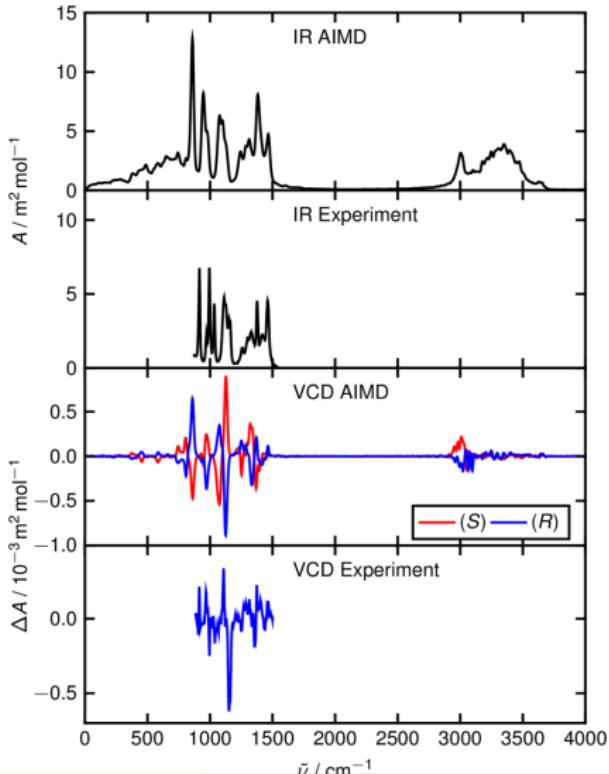


Thomas–Kirchner approach

Gas phase



Bulk phase



Summary: Vibrational spectroscopy

① Static approach (QM)

- Solve stationary Schrödinger equation
- Represent all vibrational modes as harmonic oscillators
- + High accuracy and fast (DFT)
- + Implemented in many QM codes
- Small region around (global) minimum geometry is modelled
- Only electronic ground state

② Dynamic approach (MD)

- Express vibrational spectra by correlation functions
- + Better sampling of the PES
- + Good for liquid systems and solvation
- Computationally demanding
- Reliable dipole moments and polarizabilities required (e.g. Wannier does not work for aromatic systems)