Molecular Spectroscopy. Rotational & Vibrational Spectra

Reading: Atkins, Ch. 13

Molecular spectroscopy vs. Atomic spectroscopy

electronic transition (Ch.17) +

Rotational, vibrational

$E_{\text{elec}} >> E_{\text{vib}} >> E_{\text{rot}}$
Energy of electromagnetic field: oscillating electric & magnetic disturbance

\[ E = h\nu = h \frac{c}{\lambda} \]

h; Planck constant (6.6 x 10^{-34} Js)
speed of light (c); 3 x 10^8 m/s,
wavelength (\(\lambda\)); distance between the neighboring peaks of wave,
\[ 1 \text{ Å} = 0.1 \text{ nm} = 10^{-10} \text{ m} \]
frequency (\(\nu\), Hz = 1 s^{-1}); number of times per second
\[ \lambda \nu = c \]
wavenumber (cm^{-1}, reciprocal cm), \( \nu\)-bar = \(\nu/c = 1/\lambda \)
cf) 1 eV ~ 8066 cm^{-1}

\[ \text{파장}(\lambda, \text{nm}) = 1240/\text{band gap energy (eV)} \]
Electromagnetic spectrum
Experimental spectroscopy: absorption or emission
\[ E_2 - E_1 = h\nu \]

- Absorption spectroscopy

- Emission spectroscopy
Source of radiation
- far IR: mercury arc
- IR: Nernst glower ($\text{ZrO}_2 + \text{Y}_2\text{O}_3$)
- Visible: Tungsten lamp
- UV: $\text{H}_2$, $\text{D}_2$ or $\text{Xe}$ lamp
- laser
- synchrotron radiation

Dispersing element: separating the frequencies of the radiation
- Prism, diffraction grating, monochromator
**Detectors:** radiation → electric current
- photomultiplier tube (PMT), diode (Si, Ge..), charge-coupled device (CCD).

**Sample:** cell/window materials
- UV/visible: quartz, glass..
- IR: NaCl, KBr

- **Raman spectroscopy**

Lower frequency: Stokes radiation
Higher frequency: anti-Stokes radiation
No frequency change: Rayleigh radiation

Why Laser in Raman?: quite small frequency shift (monochromator needed)
low scattered intensity
**Intensity of spectral lines**

\[ I_0 \rightarrow I \]

incident intensity \( \rightarrow \) transmitted intensity

- Transmittance \( T = \frac{I}{I_0} \)
- Beer-Lambert law \( I = I_0 10^{-\varepsilon [J] l} \)

\([J]\): molar concentration, \(l\): length,
\(\varepsilon\): molar absorption coefficient

( extinction coefficient), \(\text{Lmol}^{-1} \text{cm}^{-1}\)

or \(\text{cm}^{2}\text{mol}^{-1}\)

- Absorbance, \( A = \log[I_0/I] \), or \( A = -\log T \) (at a given wavenumber)

\( A = \varepsilon [J] l \) "optical density"
Absorption intensities

Population at equilibrium: \( \frac{N_i}{N} \propto e^{-E_i/kT} \) at T (K)

\( kT \sim 200 \text{ cm}^{-1} \) at room temperature

\[ I \propto \text{population} \propto e^{-E_i/kT} \]

\[ \frac{N_0}{N} = Ae^{-E_0/kT}, \quad \frac{N_1}{N} = Ae^{-E_1/kT} \]

\[ \rightarrow \frac{N_1}{N_0} = e^{-\left(E_1-E_0\right)/kT} \]

E2  e.g.) at room T, \( E_1 - E_0 = 200 \text{ cm}^{-1} \rightarrow \frac{N_1}{N_0} = e^{-1} \)

E1  \( E_1 - E_0 = 2000 \text{ cm}^{-1} \rightarrow \frac{N_1}{N_0} \sim 0 \)

E0

Rotation: \( E_{\text{rot}} = J(J+1) \frac{\hbar^2}{2I} \)

\( \frac{N_j}{N_0} \propto (2J + 1)e^{-E_{\text{rot}}/kT} \)
\( B_{nm} \): Einstein coefficient of stimulated absorption (B)
\( B_{mn} \): Einstein coefficient of stimulated emission (B')
\( E_m, N_m \)
\( A_{mn} \): Einstein coefficient of spontaneous emission (A)

Spontaneous emission: \(-dN_m/dt = +A_{mn}N_m\)

Stimulated emission: \(-dN_m/dt = +B_{mn}N_m \rho(\nu_{mn})\)
\( \rho \): density of radiation \( E_n, N_n \)

Stimulated absorption: \(dN_n/dt = -dN_m/dt = B_{nm}N_n \rho(\nu_{mn})\)

At equilibrium \( \uparrow = \text{rate} = \text{rate} \downarrow \)
\( B_{nm}N_n \rho(\nu_{mn}) = A_{mn}N_m + B_{mn}N_m \rho(\nu_{mn}) \)

\( N_m/N_n = B_{nm}N_n \rho(\nu_{mn}) / [A_{mn}N_m + B_{mn}N_m \rho(\nu_{mn})] = e^{-(E_m - E_n)/kT} = e^{-h\nu_{mn}/kT} \)
\[ \rho (\nu_{mn}) = \frac{A_{mn}}{B_{nm}e^{-\hbar \nu_{mn}/kT - B_{mn}}} \]  

Planck’s law
\[ \rho (\nu_{mn}) = \frac{(8\pi \hbar \nu^3/c^3)(1/e^{-\hbar \nu_{mn}/kT - B_{mn}})}{1} \]  

(1) = (2) \hspace{1cm} B_{mn} = B_{nm} = B

A/B = A_{mn}/B_{mn} = 8\pi \hbar \nu^3/c^3

\[ \nu \uparrow \rightarrow A \uparrow \text{(spontaneous emission)} \rightarrow \text{laser} \]

Lower frequency (rotational & vibrational transitions) \rightarrow A can be ignored
**Selection rules:** transition is forbidden or allowed?

transition dipole moment
Linewidths

Why? 1. experimental conditions, 2. Inherent limitations
→ To achieve high resolution, we need to know how to minimize these contributions

- Inherent limitations: Doppler broadening & lifetime broadening

(a) Doppler broadening

- Doppler effect: radiation is shifted in frequency when the source is moving towards or away from the observer
(b) **lifetime broadening**: quantum mechanical effect

System that is changing with time → impossible to specify the energy level exactly

Uncertainty broadening

Factors influencing the lifetime of excited states

→ Spontaneous emission (coefficient $A \propto \nu^3$), stimulated emission, collision, deactivation (pressure broadening)
\( \tau \downarrow \) (shorter lifetime) \( \rightarrow \) broader spectral lines
\( \rightarrow \) working at low pressure (collisional linewidth)
  low frequency transitions \( \rightarrow \) small linewidth
Pure rotation spectra: microwave region

Moment of inertia

I: moment of inertia

\[ I = \sum m_i r_i^2 \]

where \( r_i \) is the perpendicular distance of the atom \( i \) from the axis of rotation

→ depending on molecular structure:
masses & molecular geometry

→ rotational spectroscopy:
information about bond lengths & bond angles
Linear molecules: zero I around the internuclear axis

e.g., 16.1. I of H₂O around axis
Rigid rotors
Spherical rotors: 3 equal I (e.g., CH₄, SiH₄, SF₆)
Symmetric rotors: 2 equal I (e.g., NH₃, CH₃Cl, CH₃CN)
Linear rotors: 1 zero I (1 about the molecule axis) (CO₂, HCl, OCS, HCCH)
Asymmetric rotors: three different I (H₂O, H₂CO, CH₃OH)

Rotational energy levels

E = J²/2I,  \( J \): magnitude of the angular momentum (\( J(J + 1)\hbar^2 \), \( J = 0, 1, 2, \ldots \))

For a, b, c axes, \( E = E_a + E_b + E_c = J_a^2/2I_a + J_b^2/2I_b + J_c^2/2I_c \)
(a) Spherical rotors
3 equal I (e.g., CH₄, SiH₄, SF₆)

\[ E = \frac{(J_a^2 + J_b^2 + J_c^2)}{2I} = \frac{J^2}{2I} \]

\[ E_J = \frac{(J(J + 1)\hbar^2}{2I}, \quad J = 0, 1, 2,... \]

Rotational constant of the molecule, B

\[ \hbar cB = \frac{\hbar^2}{2I} \quad \text{so} \quad B = \frac{\hbar}{4\pi cI} \]

\[ \rightarrow E_J = \hbar cBJ(J + 1), \quad J = 0, 1, 2,... \]

\[ \rightarrow \text{wavenumber term, } F(J) = BJ(J + 1) \]

F(J): rotational term

\[ F(J) - F(J - 1) = 2BJ \]

\[ I \uparrow \rightarrow B \downarrow \]

Large molecules: closely spaced rotational energy levels
e.g., CCl₄, \( I = 4.85 \times 10^{-45} \text{ kgm}^2 \)

\[ \rightarrow B = 0.0577 \text{ cm}^{-1} \]
(b) Symmetric rotors
2 equal I & 1 different I (e.g., CH₃Cl, NH₃, C₆H₆):
principle axis (I₁) & other two (I₂)
If → oblate (like pancake or C₆H₆)
If → prolate (like cigar, CH₃Cl)
\[ E = \frac{J_b^2 + J_c^2}{2I_\perp} + \frac{J_a^2}{2I_\parallel} \]
\[ J^2 = J_a^2 + J_b^2 + J_c^2 \]
\[ E = \frac{(J^2 - J_a^2)}{2I_\perp} + \frac{J_a^2}{2I_\parallel} = \frac{J^2}{2I_\perp} + (\frac{1}{2I_\parallel} - \frac{1}{2I_\perp})J_a^2 \]

Quantum mechanics
\[ J^2 = (J(J + 1)\hbar^2, \quad J = 0, 1, 2,... \]
\[ J_a = K\hbar, \quad K = 0, \pm 1, \ldots \pm J \]
\[ E_{J,K} = J(J + 1)\hbar^2/2I_\perp + K^2\hbar^2/2(1/I_\parallel - 1/I_\perp) \]
\[ F(J, K) = BJ(J + 1) + (A - B)K^2 \]
With \( A = \hbar/4\pi cI_\parallel \) and \( B = \hbar/4\pi cI_\perp \)

K = 0, E depends only on I_\perp
K = ±J, F(J, K) = BJ + AJ² \quad \text{e.g., 16.2}
(c) Linear rotors
K = 0

\[ E = J(J + 1)\hbar^2/2I \quad J = 0, 1, 2, \ldots \]
\[ F(J, K) = BJ(J + 1) \]

(d) Degeneracies and the Stark effect
E of symmetric rotor depends on J & K
J, K \rightarrow M_J quantized, M_J = 0, \pm 1, \ldots, \pm J
\rightarrow (2J + 1) degeneracy

Symmetric rotor:
K \neq 0; 2(2J +1)-fold degenerate (J, K, respectively)
K = 0, (2J+1)-fold degenerate

Linear rotor (K = 0): 2J+1 fold degenerate
Spherical rotor: 2J+1 fold degenerate

Stark effect: splitting of states by an electric field
Electric field, $E$

$$E(J, M_J) = \hbar cBJ(J + 1) + a(J, M_J)\mu^2 E^2$$

where $a(J, M_J) = [J(J + 1) - 3M_J^2]/[2\hbar cBJ(J + 1)(2J - 1)(2J + 3)]$

$\mu$: permanent electric dipole moment

(e) Centrifugal distortion

Rigid rotor by centrifugal force: change $I$

Diatomic molecule

$$F(J) = BJ(J + 1) - D_J J^2(J + 1)^2$$

$D_J$: centrifugal distortion const

$$D_J = 4B^3/\sqrt{2}$$
Rotational transitions
B of small molecules $\rightarrow 0.1 \sim 10 \text{ cm}^{-1}$ (microwave region)

(a) Rotational selection rules
Gross selection rule: $\mu \neq 0$ (permanent electric dipole moment)
$\rightarrow$ for pure rotational spectrum, it must be *polar*
Homonuclear diatomic molecules,
symmetrical linear molecule (CO$_2$),
spherical rotor $\rightarrow$ rotationally inactive

Specific rotational selection rules: transition dipole moment between rotational states
For linear molecule: $\Delta J = \pm 1$, $\Delta M_J = 0$, $\pm 1$
($\Delta J = -1$: emission, $\Delta J = +1$: absorption)
$\rightarrow$ conservation of angular momentum
when a photon, a spin-1 particle, is emitted or absorbed

Symmetric rotors: $\Delta K = 0$, $\Delta J = \pm 1$
(principal axis: no change)
F(J, K) = BJ(J + 1) + (A – B)K^2

Absorption: J → J + 1; \( \nu = 2B(J + 1) \), \( J = 0, 1, 2... \)
→ 2B, 4B, 6B,…
Separation: 2B

e.g., 16.3

Intensity of rotational spectrum
I is proportional to \( N_J \): population at equilibrium
\[ N_J = N_g J \exp(-E_J/kT)/\sum g_J \exp(-E_J/kT) \]
g\(_J\): degeneracy of level J

Linear molecule: \( g_J = 2J + 1 \)
\[ E_J = \hbar c BJ(J + 1) \]
\[ N_J = N(2J + 1)\exp(-\hbar c BJ(J + 1)/kT) \]
\[ J_{\text{max}} \rightarrow N_J/dJ = 2\exp(-\hbar c BJ(J + 1)/kT) - [\hbar c B(2J + 1)^2/kT] \exp(-\hbar c BJ(J + 1)/kT) \]
\[ = [2 - \hbar c B(2J + 1)^2/kT] \exp(-\hbar c BJ(J + 1)/kT) \]
\[ J_{\text{max}} \sim (kT/2\hbar c B)^{1/2} - 1/2 \]
e.g., typical molecule at room T, \( kT \sim 1000\hbar c B \rightarrow J_{\text{max}} \sim 22 \)
Rotational Raman spectra
Selection rule: must be anisotropically polarizable

Raman effect: inelastic light scattering
anisotropically (비정방성) polarizable?

\( H_2 \)

Induced dipole moment, \( \mu = \alpha E \)
\( \alpha \): polarizability

Atom: isotropically polarizable

Spherical rotor: isotropically polarizable (정방성)
\( \rightarrow \) \( \text{CH}_4, \text{SF}_6 \): rotationally Raman inactive, rotationally (microwave) inactive

Nonspherical rotors: anisotropically polarizable (depend on the direction of \( E \))
\( \rightarrow \) diatomics, linear molecules, symmetric rotors
\( \rightarrow \) rotationally Raman active
e.g., homonuclear diatomic:
rotational inactive, but rotationally Raman active
Selection rule
Gross selection rule: anisotropic $\alpha$
Specific selection rule
- Linear rotors: $\Delta J = 0, \pm 2$
- Symmetric rotors: $\Delta J = 0, \pm 1, \pm 2; \Delta K = 0$
$\Delta J = 0$: no shift of the scattered photon’s frequency (Rayleigh line)

c.f. Why $\Delta J = \pm 2$?
i) $\mu_{\text{ind}} = \alpha E(t) = \alpha E \cos \omega_i t$, $\omega_i$: angular frequency of incident photon
If molecule is rotating at a circular frequency $\omega_R$
$\rightarrow \alpha = \alpha_0 + \Delta \alpha \cos 2\omega_R t$, where $\Delta \alpha = \alpha_{||} - \alpha_{\perp}$, $\alpha$ from $\alpha_0 + \Delta \alpha$ to $\alpha_0 - \Delta \alpha$ as the molecule rotates $\rightarrow$ “2”; 1 revolution, polarizability twice
\[
\mu_{\text{ind}} = (\alpha_0 + \Delta \alpha \cos 2\omega_R t) \times (E \cos \omega_i t) = \alpha_0 E \cos \omega_i t + E \Delta \alpha \cos 2\omega_R t \cos \omega_i t = \\
\alpha_0 E \cos \omega_i t + (1/2) E \Delta \alpha [\cos (\omega_i + 2\omega_R) t + \cos (\omega_i - 2\omega_R) t] \\
\]

\(\omega_i\), incident frequency \hspace{1cm} \omega_i \pm 2\omega_R \\
Rayleigh radiation \hspace{1cm} shifted Raman lines

ii) Raman \rightarrow 2\) photons involved (spin-1 particle) \rightarrow max. changes in angular 
    momentum quantum number = \(\pm 2\)

Raman spectrum of a linear rotor: \(\Delta J = \pm 2\)

\(\Delta J = +2, J \rightarrow J + 2\), Stokes lines

\[\bar{\nu}(J \rightarrow J + 2) = \bar{\nu}_i - [B(J + 2)(J + 3) - BJ(J + 1)] = \bar{\nu}_i - 2B(2J + 3),\ J = 0, 1, 2,...\]

Stokes lines: -6B, -10B, -14B, ...

\(\Delta J = -2, J \rightarrow J -2\), Anti-Stokes lines

\[\bar{\nu}(J \rightarrow J - 2) = \bar{\nu}_i + 2B(2J - 1),\ J = 2, 3, 4,...\]
The vibrations of diatomic molecules

Molecular vibrations
Diatomic molecule
$H_2$

Harmonic oscillator, $V = \frac{1}{2}kx^2$, $x = R - R_e$

$$-(\hbar^2/2\mu)(d^2\Psi/dx^2) + (1/2kx^2)\Psi = E\Psi$$

$\mu = m_{\text{eff}} = m_1 m_2/(m_1 + m_2)$: reduced or effective mass

$E_v = (v + 1/2)\hbar\omega$, $v = 0, 1, 2…$

$\omega = \sqrt{(k/\mu)}$, $\omega = 2\pi v \rightarrow v = (1/2\pi)\sqrt{(k/\mu)}$

Vibrational term, $G(v) = (v + 1/2)\bar{\nu}$, $E_v = \hbar c G(v)$

$\bar{\nu} = (1/2\pi c)\sqrt{(k/\mu)}$

Homonuclear diatomic molecule, $m_1 = m_2$, $\mu = 1/2m$
Selection rule
Gross selection rule: dipole moment $\mu \neq 0$
(dipole moment must change) $\rightarrow$ infrared active
Specific vibrational selection rule
\( \Delta v = +1: \) absorption, \( \Delta v = -1: \) emission
\( \Delta G_{v+1/2} = G(v + 1) - G(v) = \bar{\nu} \)

At room T, \( kT/\hbar c = 200 \text{ cm}^{-1} \rightarrow \text{IR} > 200 \text{ cm}^{-1} \)

Anharmonicity
True potential energy?
\( V(x) = V(0) + (dV/dx)_0 x + \frac{1}{2} (d^2V/dx^2)_0 x^2 + \ldots \)

One approach to anharmonicity
Morse potential energy
\( V = \hbar cD_e [1 - e^{-a(R - R_e)}]^2 \)
\( a = [m_{\text{eff}} \omega^2 / 2 \hbar c D_e]^{1/2}, \) \( D_e: \) depth of the potential minimum
\[ H = T + V, \quad H\Psi = E\Psi \]
\[ \rightarrow E_v = (v + \frac{1}{2})\hbar\nu - (v + \frac{1}{2})^2 x_e\hbar\nu + (v + \frac{1}{2})^3 y_e\hbar\nu + \ldots \]
\[ x_e = \hbar a^2/2\mu \omega = \nu/4D_e: \text{anharmonicity constant} \]

\[ G(v) = (v + \frac{1}{2})\nu - (v + \frac{1}{2})^2 x_e\nu + \ldots, \quad v = 0, 1, 2, \ldots v_{\text{max}} \]

Wavenumbers of transitions with \( \Delta v = +1 \)
\[ \Delta G_{v+1/2} = G(v + 1) - G(v) = \nu - 2(v + 1)x_e\nu + \ldots \]
(or \( \Delta E (v \rightarrow v + 1) = \hbar\nu - 2(v + 1)x_e\hbar\nu + \ldots \))
\[ \rightarrow \text{when } x_e \neq 0, \text{the transitions move to lower wavenumbers as } v \text{ increases} \]

Mainly \( \Delta v = \pm 1 \) (fundamental frequency), however, anharmonicity allows additional weak lines corresponding \( \Delta v = \pm 2, \pm 3, \ldots \) (“overtones”)

1st overtone, \( G(v + 2) - G(v) = 2\nu - 2(2v + 3)x_e\nu + \ldots \)

Selection rule is derived from harmonic oscillator, for an anharmonic oscillator, all values of \( \Delta v \) are allowed, but transitions with \( \Delta v > 1 \) are weak if the anharmonicity is slight
**Vibration-rotation spectra**
Each line of high-resolution vib. Spectrum of heteronuclear diatomic molecular consists of large # of closely spaced lines ("band spectra") → rotational transition with vibrational transition

\[ E = E_{\text{vib}} + E_{\text{rot}} + E_{\text{ele}}, \quad E_{\text{ele}} > E_{\text{vib}} > E_{\text{rot}} \]

IR radiation → no electronic transition, vib. transition + rotational transition

**Diatomic molecule**

\[ E_{v,J} = (v + \frac{1}{2})h\nu + hcBJ(J + 1) \quad \text{H.O.} \]
\[ E_{v,J} = (v + \frac{1}{2})h\nu - (v + \frac{1}{2})2x_eh\nu + hcBJ(J + 1) \quad \text{Anharm.} \]

**Vibration-rotation term**
\[ S(v,J) = G(v) + F(J) \]
Selection rule $\mu \neq 0$
\[ \Delta v = \pm 1, \]
\[ \Delta J = \pm 1, 0 \quad (\text{total orbital ang. momentum about internuclear axis } \neq 0, \wedge \neq 0) \]
e.g., paramagnetic molecule, NO

\[ \Delta v = 1 \quad (v \rightarrow v + 1) \]
i) $\Delta J = -1, \Delta E = h\nu - 2BJ, \quad \nu_p(J) = S(v+1, J-1) - S(v, J) = \nu - 2BJ \]
\[ \rightarrow h\nu - 2B, h\nu - 4B,... \quad \text{P-branch} \]
ii) $\Delta J = 0, \Delta E = h\nu, \quad \nu_Q(J) = S(v+1, J) = \nu \quad \text{Q-branch} \]
\[ \text{allowed: NO, forbidden: HCl} \]
iii) $\Delta J = +1, \Delta E = h\nu + 2B(J + 1), \quad \nu_R(J) = S(v+1, J+1) - S(v, J) = \nu + 2B(J + 1) \quad \text{R-branch} \]
Vibrational Raman spectra of diatomic molecule
Gross selection rule: polarizability should change as the molecule vibrates
Homonuclear and heteronuclear diatomic molecules → vibrational Raman active
Specific selection rule: $\Delta v = \pm 1, \; \Delta J = 0, \; \pm 2$
$\Delta v = +1$
  i) $\Delta J = -2$, O-branch
  ii) $\Delta J = 0$, Q-branch
  iii) $\Delta J = +2$, S-branch
The vibrations of polyatomic molecules
Diatomic molecule: one mode of vibration → bond stretch
Polyatomic molecules: several modes

\(N\) atoms \(\rightarrow\) degree of freedom for vibration (p. 522, Justification 16.9)

\(f_v\) linear \(3N - 5\) (total: \(3N, 3\) translation, 2 rotation)

\(f_v\) nonlinear \(3N - 6\) (total: \(3N, 3\) translation, 3 rotation)

\(\text{CO}_2\) (linear molecule), \(f_v = 3 \times 3 - 5 = 4\) modes for vibration

Symmetric stretch, \(\nu_1 = 1388\ \text{cm}^{-1}\) (IR inactive)

Antisymmetric stretch, \(\nu_3 = 2349\ \text{cm}^{-1}\)

Bending, \(\nu_2 = 667\ \text{cm}^{-1}\) (degenerate)

\(\nu(\text{bending}) < \nu(\text{stretch})\)

\[G_p(v) = (v + \frac{1}{2})\nu_q, \quad \nu_q = (1/2\pi c)\sqrt{(k_q/m_q)}\]
$H_2O$, $f_v = 3 \times 3 - 6 = 3$ modes

Gross selection rule for IR: change of dipole moment
  e.g., symmetric stretch of CO$_2$: no dipole moment change $\rightarrow$ IR inactive
  antisymmetric stretch, bending modes $\rightarrow$ IR active

Specific selection rule $\Delta v_q = \pm 1$ in harmonic approximation

Molecules can be identified from characteristic frequencies and intensities
Vibrational Raman spectra of polyatomic molecules
Vibrational modes are Raman active if changing polarizability
e.g., symmetric stretch of CO$_2$: Raman active

Exclusion rule: if the molecule has a centre of symmetry, then no modes can be both
IR and Raman active

Depolarization ratio, $\rho$
The ratio of intensities of the scattered light with polarization perpendicular and
parallel to the plane of polarization of the incident radiation

$$\rho = \frac{I_\perp}{I_\parallel}$$

Measuring $\rho$: polarizing filter
If emergent light is not polarized: $\rho \sim 1$
$\rho \geq 0.75$: depolarized, $\rho < 0$: polarized