

Molecular Spectroscopy. Rotational & Vibrational Spectra

Reading: Atkins, Ch. 13

Molecular spectroscopy vs.
electronic transition (Ch.17) +
Rotational, vibrational

Atomic spectroscopy
electronic transition

$$E_{\text{elec}} \gg E_{\text{vib}} \gg E_{\text{rot}}$$

Energy of electromagnetic field: oscillating electric & magnetic disturbance

$$E = h\nu = h c/\lambda$$

h; Planck constant (6.6×10^{-34} Js)

speed of light (c); 3×10^8 m/s,

wavelength (λ); distance between the neighboring peaks of wave,

$$1 \text{ \AA} = 0.1 \text{ nm} = 10^{-10} \text{ m}$$

frequency (ν , Hz = 1 s^{-1}); number of times per second

$$\lambda\nu = c$$

wavenumber (cm^{-1} , reciprocal cm), $\bar{\nu} = \nu/c = 1/\lambda$

cf) $1 \text{ eV} \sim 8066 \text{ cm}^{-1}$

$$\text{파장}(\lambda, \text{ nm}) = 1240/\text{band gap energy (eV)}$$

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: H_2 , D_2 or 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**

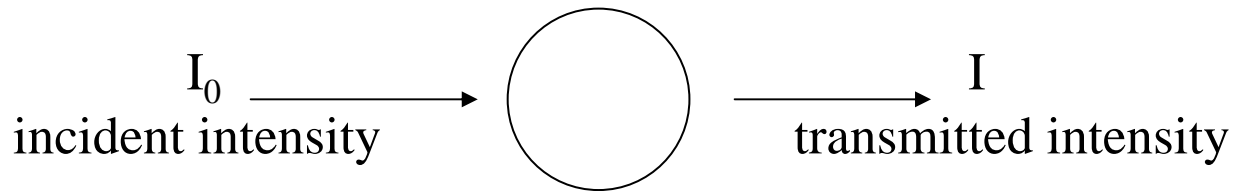
Lower frequency: Stokes radiation

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



- Transmittance $T = I/I_0$

- Beer-Lambert law $I = I_0 10^{-\epsilon[J]l}$

[J]: molar concentration, l : length,

ϵ : molar absorption coefficient

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

or $\text{cm}^2\text{mol}^{-1}$

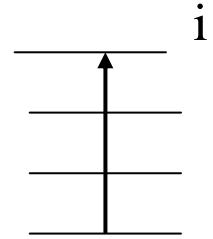
- Absorbance, $A = \log[I_0/I]$, or $A = -\log T$ (at a given wavenumber)

$A = \epsilon[J]l$ “optical density”

Absorption intensities

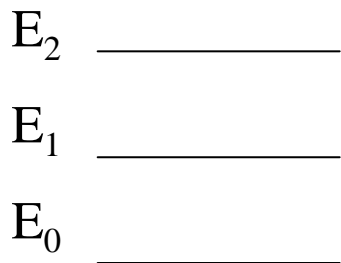
Population at equilibrium $N_i/N \propto e^{-E_i/kT}$ at T (K)
 $kT \sim 200 \text{ cm}^{-1}$ at room temperature

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

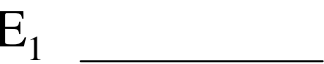


$$N_0/N = Ae^{-E_0/kT}, \quad N_1/N = Ae^{-E_1/kT}$$

$$\rightarrow N_1/N_0 = e^{-(E_1-E_0)/kT}$$



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



$E_1 - E_0 = 2000 \text{ cm}^{-1} \rightarrow N_1/N_0 \sim 0$



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

$$N_J/N_0 \propto (2J + 1)e^{-E_{\text{rot}}/kT}$$

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: $-dN_m/dt = +A_{mn}N_m$

B_{nm}

$B_{mn} A_{mn}$

Stimulated emission: $-dN_m/dt = +B_{mn}N_m\rho(v_{mn})$

ρ : density of radiation E_n, N_n

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

At equilibrium rate $\uparrow =$ rate \downarrow

$$B_{nm}N_n \rho(v_{mn}) = A_{mn}N_m + B_{mn}N_m\rho(v_{mn})$$

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

$$\rho(\nu_{mn}) = A_{mn} / (B_{nm} e^{-h\nu_{mn}/kT} - B_{mn}) \quad (1)$$

Planck's law

$$\rho(\nu_{mn}) = (8\pi h \nu^3 / c^3) (1 / e^{-h\nu_{mn}/kT} - B_{mn}) \quad (2)$$

$$(1) = (2) \quad B_{mn} = B_{nm} = B$$

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

$\nu \uparrow \rightarrow A \uparrow$ (spontaneous emission) \rightarrow 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

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

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)

$$E = (J_a^2 + J_b^2 + J_c^2)/2I = J^2/2I$$

$$E_J = (J(J + 1)\hbar^2/2I), \quad J = 0, 1, 2, \dots$$

Rotational constant of the molecule, B

$$hcB = \hbar^2/2I \quad \text{so } B = \hbar/4\pi cI$$

$$\rightarrow E_J = hcBJ(J + 1), \quad J = 0, 1, 2, \dots$$

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

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 x 10⁻⁴⁵ kgm²

$$\rightarrow B = 0.0577 \text{ cm}^{-1}$$

(b) Symmetric rotors

2 equal I & 1 different I (e.g., CH₃Cl, NH₃, C₆H₆):

principle axis (I_{II}) & other two (I_⊥)

If → oblate (like pancake or C₆H₆)

If → prolate (like cigar, CH₃Cl)

$$E = (J_b^2 + J_c^2)/2I_{\perp} + J_a^2/2I_{II}$$

$$J^2 = J_a^2 + J_b^2 + J_c^2$$

$$E = (J^2 - J_a^2)/2I_{\perp} + J_a^2/2I_{II} = J^2/2I_{\perp} + (1/2I_{II} - 1/2I_{\perp})J_a^2$$

Quantum mechanics

$$J^2 = J(J + 1)\hbar^2, \quad J = 0, 1, 2, \dots$$

$$J_a = K\hbar, \quad K = 0, \pm 1, \dots, \pm J$$

$$E_{J,K} = J(J + 1)\hbar^2/2I_{\perp} + K^2\hbar^2/2(1/I_{II} - 1/I_{\perp})$$

$$F(J, K) = BJ(J + 1) + (A - B)K^2$$

With $A = \hbar^2/4\pi c I_{II}$ and $B = \hbar^2/4\pi c I_{\perp}$

$K = 0$, E depends only on I_⊥

$K = \pm J$, $F(J, K) = BJ + AJ^2$ e.g., 16.2

(c) Linear rotors

$$K = 0$$

$$E = J(J + 1)\hbar^2/2I \quad J = 0, 1, 2, \dots$$

$$F(J, K) = BJ(J + 1)$$

(d) Degeneracies and the Stark effect

E of symmetric rotor depends on J & K

J, K \rightarrow M_J quantized, $M_J = 0, \pm 1, \dots, \pm J$

\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

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

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

μ : 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

$$D_J = 4B^3/\bar{V}^2$$

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: $J \rightarrow J + 1$; $\bar{\nu} = 2B(J + 1)$, $J = 0, 1, 2, \dots$

$\rightarrow 2B, 4B, 6B, \dots$

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: $g_J = 2J + 1$

$$E_J = hcBJ(J + 1)$$

$$N_J = N(2J + 1) \exp(-hcBJ(J + 1)/kT)$$

$$J_{\max} \rightarrow N_J/dJ = 2 \exp(-hcBJ(J + 1)/kT) - [hcB(2J + 1)^2/kT] \exp(-hcBJ(J + 1)/kT)$$

$$= [2 - hcB(2J + 1)^2/kT] \exp(-hcBJ(J + 1)/kT)$$

$$J_{\max} \sim (kT/2hcB)^{1/2} - 1/2$$

e.g., typical molecule at room T, $kT \sim 1000hcB \rightarrow J_{\max} \sim 22$

Rotational Raman spectra

Selection rule: must be anisotropically polarizable

Raman effect: inelastic light scattering

anisotropically (비정방성) polarizable?

H₂

Induced dipole moment, $\mu = \alpha E$

α : polarizability

Atom: isotropically polarizable

Spherical rotor: isotropically polarizable (정방성)

→ CH₄, SF₆: rotationally Raman inactive, rotationally (microwave) inactive

Nonspherical rotors: anisotropically polarizable (depend on the direction of E)

→ diatomics, linear molecules, symmetric rotors

→ rotationally Raman active

e.g., homonuclear diatomic:

rotational inactive, but rotationally Raman active

Selection rule

Gross selection rule: anisotropic α

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) $\mu_{\text{ind}} = \alpha E(t) = \alpha E \cos \omega_i t$, ω_i : angular frequency of incident photon

If molecule is rotating at a circular frequency ω_R

$\rightarrow \alpha = \alpha_0 + \Delta\alpha \cos 2\omega_R t$, where $\Delta\alpha = \alpha_{\parallel} - \alpha_{\perp}$, α from $\alpha_0 + \Delta\alpha$ to $\alpha_0 - \Delta\alpha$ as the molecule rotates \rightarrow "2"; 1 revolution, polarizability twice

$$\rightarrow \mu_{\text{ind}} = (\alpha_0 + \Delta\alpha \cos 2\omega_R t) \times (E \cos \omega_i t) = \alpha_0 E \cos \omega_i t + E \Delta\alpha \cos 2\omega_R t \cos \omega_i t =$$

$$\alpha_0 E \cos \omega_i t + (1/2) E \Delta\alpha [\cos(\omega_i + 2\omega_R)t + \cos(\omega_i - 2\omega_R)t]$$

\downarrow
 ω_i , incident frequency
 Rayleigh radiation

\downarrow
 $\omega_i \pm 2\omega_R$
 shifted Raman lines

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

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

$\Delta J = +2$, $J \rightarrow J + 2$, Stokes lines

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

Stokes lines: $-6B, -10B, -14B, \dots$

$\Delta J = -2$, $J \rightarrow J - 2$, Anti-Stokes lines

$$\bar{\nu}(J \rightarrow J - 2) = \bar{\nu}_i + 2B(2J - 1), J = 2, 3, 4, \dots$$

The vibrations of diatomic molecules

Molecular vibrations

Diatomic molecule

H₂

Harmonic oscillator, $V = 1/2kx^2$, $x = R - R_e$

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

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

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

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

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

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

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, $kT/hc = 200 \text{ cm}^{-1} \rightarrow \text{IR} > 200 \text{ cm}^{-1}$

Anharmonicity

True potential energy?

$$V(x) = V(0) + (dV/dx)_0 x + \frac{1}{2}(d^2V/dx^2)_0 x^2 + \dots$$

One approach to anharmonicity

Morse potential energy

$$V = hcD_e[1 - e^{-a(R - R_e)}]^2$$

$a = [m_{\text{eff}}\omega^2/2hcD_e]^{1/2}$, D_e : depth of the potential minimum

$$H = T + V, H\Psi = E\Psi$$

$$\rightarrow E_v = (v + 1/2)h\nu - (v + 1/2)^2 x_e h\nu + (v + 1/2)^3 y_e h\nu + \dots$$

$$x_e = \hbar a^2 / 2\mu\omega = \bar{\nu} / 4D_e: \text{anharmonicity constant}$$

$$G(v) = (v + 1/2)\bar{\nu} - (v + 1/2)^2 x_e \bar{\nu} \dots, \quad v = 0, 1, 2, \dots, v_{\max}$$

Wavenumbers of transitions with $\Delta v = +1$

$$\Delta G_{v+1/2} = G(v + 1) - G(v) = \bar{\nu} - 2(v + 1)x_e \bar{\nu} + \dots$$

(or $\Delta E (v \rightarrow v + 1) = h\nu - 2(v + 1)x_e h\nu \dots$)

\rightarrow when $x_e \neq 0$, the transitions move to lower wavenumbers as v increases

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

$$1^{\text{st}} \text{ overtone, } G(v + 2) - G(v) = 2\bar{\nu} - 2(2v + 3)x_e \bar{\nu} + \dots$$

Selection rule is derived from harmonic oscillator, for an anharmonic oscillator, all values of Δv 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

$$E_{\text{v},J} = (v + \frac{1}{2})h\nu + hcBJ(J + 1) \quad \text{H.O.}$$

$$E_{\text{v},J} = (v + \frac{1}{2})h\nu - (v + \frac{1}{2})2x_e h\nu + hcBJ(J + 1) \quad \text{Anharm.}$$

Vibration-rotation term

$$S(\text{v},J) = G(\text{v}) + F(J)$$

Selection rule $\mu \neq 0$

$$\Delta v = \pm 1,$$

$\Delta J = \pm 1, 0$ (total orbital ang. momentum about internuclear axis $\neq 0, \Lambda \neq 0$)

e.g., paramagnetic molecule, NO

$$\Delta v = 1 (v \rightarrow v + 1)$$

i) $\Delta J = -1, \Delta E = h\nu - 2BJ, \bar{\nu}_p(J) = S(v+1, J-1) - S(v, J) = \bar{\nu} - 2BJ$
 $\rightarrow h\nu - 2B, h\nu - 4B, \dots$ P-branch

ii) $\Delta J = 0, \Delta E = h\nu, \bar{\nu}_Q(J) = S(v+1, J) = \bar{\nu}$ Q-branch

allowed: NO, forbidden: HCl

iii) $\Delta J = +1, \Delta E = h\nu + 2B(J + 1), \bar{\nu}_R(J) = S(v+1, J+1) - S(v, J) = \bar{\nu} + 2B(J + 1)$
R-branch

Vibrational Raman spectra of diatomic molecule

Gross selection rule: polarizability should change as the molecule vibrates

Homonuclear and heteronuclear diatomic molecules \rightarrow 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 \rightarrow 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)

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

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)

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

$$G_p(\nu) = (\nu + 1/2)\bar{\nu}_q, \quad \bar{\nu}_q = (1/2\pi c)\sqrt{(k_q/m_q)}$$

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 CO₂: Raman active

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

Depolarization ratio, ρ

The ratio of intensities of the scattered light with polarization perpendicular and parallel to the plane of polarization of the incident radiation

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

Measuring ρ : polarizing filter

If emergent light is not polarized: $\rho \sim 1$

$\rho \geq 0.75$: depolarized, $\rho < 0$: polarized