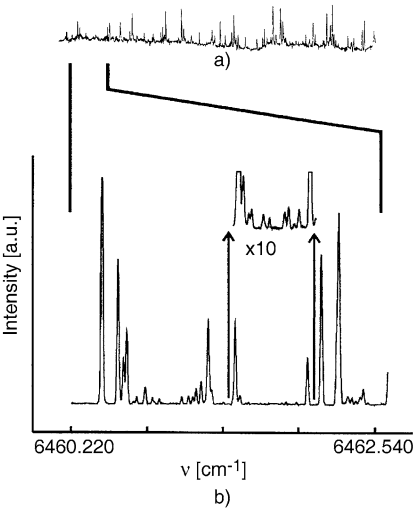


Fig. 1.63 Comparison of overtone spectra of C_2H_2 around $\lambda = 1.5$ μm, measured (**a**) with a Fourier spectrometer and (**b**) with a color-center laser and intracavity optoacoustic spectroscopy [74]

center laser and photo-acoustic spectroscopy (Fig. 1.63b). Weak lines, which are barely seen in the Fourier spectrum, still have a large signal-to-noise ratio in the optoacoustic spectrum as shown by the insert in Fig. 1.63b [74].

1.10 Problems

1.1 A monochromatic laser beam is sent through a sample of diatomic molecules. The laser wavelength is tuned to a vibration–rotation transition $(v'', J'') \rightarrow (v', J')$ with an absorption cross section of $\sigma_{ik} = 10^{-18}$ cm^2.

(a) Estimate the fraction n_i/n of molecules in the level $(v_i'' = 0, J_i'' = 20)$ for thermal equilibrium at $T = 300$ K (vibrational constant $\omega_e = 200$ cm^{-1}, rotational constant $B_e = 1.5$ cm^{-1}).
(b) Calculate the absorption coefficient for a total gas pressure of 10 mbar.
(c) What is the transmitted laser power P_T behind an absorption path length of 10 cm for an incident power $P_0 = 100$ mW?

1.2 A focused laser beam ($\varnothing = 0.4$ mm) with 1-mW input power at $\lambda = 623$ nm crosses a molecular beam ($\varnothing = 1$ mm) perpendicularly. The absorbing molecules with a partial flux density $N_i = n_i \cdot \bar{v} = 10^{12}/(\text{s cm}^2)$ and a velocity $\bar{v} = 5 \times 10^4$ cm/s have the absorption cross section $\sigma = 10^{-16}$ cm^2.

How many photoelectrons are counted with a photomultiplier if the fluorescence emitted from the crossing volume $V_c = 10^{-4}$ cm^3 of both the laser and molecular beams is imaged by a lens with $D = 4$ cm at a distance $L = 8$ cm from V_c onto the photocathode with quantum efficiency $\eta_{ph} = 0.2$?

1.3 A monochromatic laser beam with $P = 1$ mW is sent through a 1 m long sample cell filled with absorbing molecules. The absorbing transition has the Doppler width $\Delta\omega_D = 2\pi \times 10^9$ s^{-1} and a peak absorption $\alpha(\omega_0) = 10^{-8}$ cm^{-1}. The laser frequency $\omega_L = \omega_0 + \Delta\omega \cdot \cos 2\pi f t$ is modulated ($\Delta\omega = 2\pi \times 10$ MHz). A detector measures the transmitted laser power P_T. Calculate the maximum ac amplitude of the detector output signal for a detector with a sensitivity of 1 V/mW. How large is the dc background signal?

1.4 How many ions per second are formed by resonant two-step photoionization if the transition $|i\rangle \rightarrow |k\rangle$ of the first step is saturated, the lifetime τ_k of the level $|k\rangle$ is $\tau_k = 10^{-8}$ s, the ionization probability by the second laser is 10^7 s^{-1}, and the diffusion rate of molecules in the absorbing level $|i\rangle$ into the excitation volume is $dN_i/dt = 10^5$/s?

1.5 A thermal detector (bolometer area 3×3 mm^2) is hit by a molecular beam with a density of $n = 10^8$ molecules per cm^3, having a mean velocity $\langle v\rangle = 4 \times 10^4$ cm/s and a mass $m = 28$ AMU. All impinging molecules are assumed to stick at the surface of the detector.

(a) Calculate the energy transferred per second to the bolometer.
(b) What is the temperature rise ΔT, if the heat losses of the bolometer are $G = 10^{-8}$ W/K?
(c) The molecular beam is crossed by an infrared laser ($\lambda = 1.5$ μm) with $P_0 = 10$ mW. The absorption coefficient is $\alpha = 10^{-10}$ cm^{-1} and the absorption path length $L = 10$ cm (by the multiple-reflection techniques). Calculate the additional temperature rise of the bolometer.

1.6 The frequency ν_0 of a molecular transition to an upper level $|k\rangle$ is 10^8 Hz below the frequency ν_L of a fixed laser line. Assume that the molecules have no magnetic moment in the ground state, but $\mu = 0.5\mu_B$ ($\mu_B = 9.27 \times 10^{-24}$ J/T) in the upper state. What magnetic field $\boldsymbol{B}$ is necessary to tune the absorption line into resonance with the laser line? How many Zeeman components are observed, if the lower level has the rotational quantum number $J = 1$ and the upper $J = 2$, and the laser is (a) linearly and (b) circularly polarized?

1.7 For velocity-modulation spectroscopy an ac voltage of 2 kV peak-to-peak and $f = 1$ kHz is applied along a discharge tube with 1 m length in the z-direction.

(a) How large is the mean electric field strength?
(b) Estimate the value of Δv_t for the ion velocity $v = v_0 + \Delta v_z \sin 2\pi f t$ for ions with the mass $m = 40$ amu (1 amu $= 1.66 \times 10^{-27}$ kg) if their mean free path length is $\Lambda = 10^{-3}$ m and the density of neutral species in the discharge tube is $n = 10^{17}$/cm^3.
(c) How large is the maximum modulation $\Delta\nu$ of the absorption frequency $\nu(v_t) = \nu_0 + \Delta\nu(v_t)$ for $\nu_0 = 10^{14}$ s^{-1}?

(d) How large is the ac signal for an absorbing transition with $\alpha(\nu_0) = 10^{-6}$ cm^{-1} if the incident laser power is 10 mW and the detector sensitivity 1 V/mW?

1.8 An absorbing sample in a cell with $L = 4$ cm is placed within the laser resonator with a total resonator loss of 2 % per round trip and a transmission $T = 0.5$ % of the output coupler.

(a) Calculate the relative decrease of the laser output power of 1 mW when the laser is tuned from a frequency ν where $\alpha = 0$ to a frequency ν_0 where the sample has an absorption coefficient $\alpha = 5 \times 10^{-8}$ cm^{-1}, while the unsaturated gain $g_0 = 4 \times 10^{-2}$ of the active laser medium stays constant.
(b) How many fluorescence photons are emitted if the fluorescence yield of the sample is 0.5 and the laser wavelength is 500 nm?
(c) Could you design the optimum collection optics that image a maximum ratio of the fluorescence light onto the photomultiplier cathode of 40 mm ∅? How many photon counts are observed if the quantum yield of the cathode is $\eta = 0.15$?
(d) Compare the detection sensitivity of (c) (dark current of the PM is 10^{-9} A) with that of method (a) if the laser output is monitored by a photodiode with a sensitivity of 10 V/W and a noise level of 10^{-9} V.

1.9 Derive Eq. (1.46).

1.10 The expanding plasma plume of evaporated material emits fluorescence when excited on an aluminium line at $\lambda = 555$ nm and on a copper line at $\lambda = 324$ nm. The intensity ratio of the total LIF excited by these lines is 1:4. The ratio of the two transition probabilities is 1:6. Calculate the relative abundance of the two atomic species.

experiments allow a very small upper limit for a possible variation with time for the values of the fine-structure constant or the Rydberg constant. Tuning the laser frequency over both transitions of hydrogen and deuterium atoms gives an accurate value of the isotope shift of the deuterium atom. The achievable $1S$–$2S$ linewidth is about 1 kHz, limited by transit-time broadening. The uncertainty of determining the line center is below 30 Hz!

2.7 Conclusion

The few examples shown above illustrate that nonlinear spectroscopy represents an important branch of laser spectroscopy of atoms and molecules. Its advantages are the Doppler-free spectral resolution if narrow-band lasers are used and the possibilities to reach high-lying states by multiphoton absorption with pulsed or cw lasers. Because of its relevance for molecular physics, numerous books and reviews cover this field. The references [203, 205, 281–289] represent only a small selection.

In combination with double-resonance techniques, nonlinear spectroscopy has contributed particularly to the assignment of complex spectra and has therefore considerably increased our knowledge about molecular structure and dynamics. This subject is covered in Chap. 5.

2.8 Problems

2.1

(a) A collimated sodium beam is crossed by the focussed beam (focal area $A = 0.2 \times 0.01$ cm^2) of a single-mode cw dye laser, tuned to the hyperfine component ($F' = 2 \leftarrow F'' = 1$) of the D_2 transition $3\,^2P_{3/2} \leftarrow 3\,^2S_{1/2}$ of Na. Calculate the saturation intensity I_s if the mean velocity of sodium atoms is $\bar{v} = 5 \times 10^4$ cm/s. The lifetime τ_K of the upper level is $\tau_K = 16$ ns and the residual Doppler width can be neglected.

(b) How large is I_s in a sodium cell at $P_{Na} = 10^{-6}$ mbar with $P_{Ar} = 10$ mbar additional argon pressure? The pressure broadening is 25 MHz/mbar for Na–Ar collisions.

2.2 A pulsed dye laser with the pulse length $\Delta T = 10^{-8}$ s and with a peak power of $P = 1$ kW at $\lambda = 600$ nm illuminates sample in a cell at $p = 1$ mbar and $T = 300$ K. A rectangular intensity profile is assumed with a laser-beam cross section of 1 cm^2. Which fraction of all N_i in the absorbing lower level $|i\rangle$ is excited when the laser is tuned to a weak absorbing transition $|i\rangle \rightarrow |k\rangle$ with the absorption cross section $\sigma_{ik} = 10^{-18}$ cm^2? The laser bandwidth is assumed to be 3 times the Doppler width.

2.3 In an experiment on polarization spectroscopy the circularly polarized pump laser causes a change $\Delta\alpha = \alpha^+ - \alpha^- = 10^{-2}\alpha_0$ of the absorption coefficient. By

which angle is the plane of polarization of the linearly polarized probe laser beam at $\lambda = 600$ μm tuned after passing through the pumped region with length L, if the absorption without pump laser $\alpha_0 L = 5 \times 10^{-2}$?

2.4 Estimate the fluorescence detection rate (number of detected fluorescence photons/s) on the Na transition $5s \rightarrow 3p$, obtained in the Doppler-free free-photon experiment of Fig. 2.32, when a single-mode dye laser is tuned to $\nu/2$ of the transition $3s \rightarrow 5s$ ($\nu = 1 \times 10^{15}$ s^{-1}) in a cell with a Na density of $n = 10^{12}$ cm^{-3}. The laser power is $P = 100$ mW, the beam is focused to the beam waist $w_0 = 10^{-2}$ cm and a length $L = 1$ cm around the focus is imaged with a collection efficiency of 5 % onto the fluorescence detector. The absorption cross section is $\sigma = a \cdot I$ with $a = 10^{-10}$ W^{-1} and the transition probability of the $5s \rightarrow 3p$ transition is $A_{ki} = 0.2(A_k + R_{\text{coll}})$.

2.5 The saturation spectrum of the Na D_1 transition $3\,^2S_{1/2} \rightarrow 3\,^2P_{1/2}$ shows the resolved hyperfine components. Estimate the relative magnitude of the cross-over signal between the two transitions $3\,^2S_{1/2}(F'' = 1) \rightarrow 3\,P_{1/2}$ ($F' = 1$ and $F' = 2$) sharing the same lower level, if the laser intensity is 2 times the saturation intensity I_s for the transition to $F' = 1$.

2.6 Which fraction of H atoms in the $1\,^2S_{1/2}$ ground state that can be excited by a Doppler-free two-photon transition into the $2\,^2S_{1/2}$ state in a collimated H atomic beam with $\overline{v} = 10^3$ m/s, when a laser with $I = 10^3$ W/cm^2 and a rectangular beam cross section of 1×1 mm^2 crosses the atomic beam perpendicularly and the absorption probability is $P_{if} = (\sigma_0 \cdot I)^2/(\gamma \cdot h\nu)^2$ where $\sigma_0 = 10^{-18}$ cm^2 and γ is the linewidth.

Solutions

Chapter 1

1. (a)

$$n_i = n \cdot \frac{(2J_i + 1)}{Z_{\text{rot}} \cdot Z_{\text{vib}}} \cdot \mathrm{e}^{-E_{\text{rot}}/kT} \cdot \mathrm{e}^{-E_{\text{vib}}/kT}$$

where $Z_{\text{rot}} = \sum_{J=0}^{\infty}(2J+1)\mathrm{e}^{-J(J+1)hcB/kT} \approx \frac{kT}{h \cdot c \cdot B}$ is the rotational partition function and $Z_{\text{vib}} = \sum_{v=0}^{\infty} \mathrm{e}^{-hc\omega_{\text{e}}(v+\frac{1}{2})/kT}$ the vibrational partition function.

For $T = 300\ \text{K} \Rightarrow kT = 4.1 \times 10^{-21}$ J.

For $J_i'' = 20 \Rightarrow E_{\text{rot}} = hcBeJ_i''(J_i''+1) \approx 1.25 \times 10^{-20}$ J

$$\Rightarrow \quad \exp[-E_{\text{rot}}/kT] = \exp[-3.05] = 4.7 \times 10^{-2}$$

$$\exp[-E_{\text{vib}}/kT] = 0.617 \quad \text{for } v'' = 0$$

$$\Rightarrow \quad \exp[-E_{\text{vib}}/kT] = 0.235 \quad \text{for } v'' = 1 \quad \text{and} \quad 0.09 \quad \text{for } v'' = 2$$

$$\Rightarrow \quad Z_{\text{vib}} \approx 1.1; \quad Z_{\text{rot}} = \frac{4.1 \times 10^{-21}}{hcB} = 138$$

$$\Rightarrow \quad \frac{n_i}{n} = \frac{41}{138 \cdot 1.1} \cdot 4.7 \times 10^{-2} \cdot 0.617 = 7.8 \times 10^{-3}.$$

(b) The absorption coefficient α is

$$\alpha_{ik} = n_i \cdot \sigma_{ik}.$$

At $p = 10\ \text{mb} \Rightarrow n \approx 2.5 \times 10^{19}/\text{cm}^3$

$$\Rightarrow \quad n_i = 2 \times 10^{17}/\text{cm}^3$$

$$\Rightarrow \quad \alpha_{ik} = 2 \times 10^{17} \times 10^{-18}\ \text{cm}^{-1} = 0.2\ \text{cm}^{-1}.$$

(c)

$$P_{\text{t}} = P_i \mathrm{e}^{-\alpha x} = 100 \cdot \mathrm{e}^{-2}\ \text{mW} = 13.5\ \text{mW}.$$

W. Demtröder, *Laser Spectroscopy 2*, DOI 10.1007/978-3-662-44641-6

2. The molecular density in the beam is

$$n_i = N_i/v = 10^{12}/\left(5\times 10^4\right)\ \mathrm{cm}^{-3} = 2\times 10^7/\mathrm{cm}^3.$$

The absorption coefficient is

$$\alpha_i = n_i\sigma_i = 2\times 10^7\times 10^{-16}\ \mathrm{cm}^{-1} = 2\times 10^{-9}\ \mathrm{cm}^{-1}.$$

At a pathlength of 1 mm the absorbed power is

$$P_0 - P_\mathrm{t} = P_0\left(1-\mathrm{e}^{-\alpha x}\right) = P_0\times 2\times 10^{-10} = 2\times 10^{-13}\ \mathrm{W}.$$

This corresponds at $\lambda = 623$ nm to

$$n_\mathrm{ph} = 2\times 10^{-13}/(h\nu) = 2\times 10^{-13}\lambda/(hc) = 6.3\times 10^5\ \text{absorbed photons/s}.$$

Each absorbed photon causes a fluorescence photon. With a collection efficiency of

$$\delta = \left(\frac{1}{4}\pi D^2\Big/L^2\right)\Big/4\pi = 1/64,\quad \eta = 0.2$$

$$\Rightarrow\quad n_\mathrm{ph\,el} = 0.2\times\frac{1}{64}\times 6.3\times 10^5 = 1.96\times 10^3\ /\mathrm{s}$$

i.e. about 2000 photoelectrons/s are produced.

3. The transmitted peak power at ω_0 is

$$P_\mathrm{t}(\omega_0) = P_0\cdot\mathrm{e}^{-\alpha\cdot L} = P_0\cdot\mathrm{e}^{-10^{-6}} \approx P_0\left(1-10^{-6}\right) \approx P_0 = 1\ \mathrm{mW}.$$

The dc signal is then $S_\mathrm{DC} = 1$ V.

The absorption changes for $\omega \neq \omega_0$, according to the Doppler profile

$$\alpha(\omega) = \alpha(\omega_0)\cdot\mathrm{e}^{-\left(\frac{\omega-\omega_0}{0.36\delta\omega_0}\right)^2}.$$

With $\delta\omega_0 = 2\pi\times 10^9\ \mathrm{s}^{-1}$ and $(\omega-\omega_0) = 2\pi\times 10^8\ \mathrm{s}^{-1}$ we obtain

$$\alpha(\omega) = \alpha(\omega_0)\cdot\mathrm{e}^{-\left(\frac{0.1}{0.36}\right)^2} \approx \alpha(\omega_0)\cdot(1-0.08) = 0.92\alpha(\omega_0)$$

$$\Rightarrow\quad \alpha(\omega_0)-\alpha(\omega) = 0.08\alpha(\omega_0)$$

$$\Rightarrow\quad P_\mathrm{t}(\omega) = P_0\cdot\mathrm{e}^{-8\times 10^{-8}} \approx P_0\left(1-8\times 10^{-8}\right).$$

The ac signal is then

$$S(\Delta\omega) = \left[P_\mathrm{t}(\omega)-P_\mathrm{t}(\omega_0)\right] = P_0\left(10^{-6}-8\times 10^{-8}\right)\ \mathrm{V}$$
$$= 0.92\times 10^{-6}P_0 = 9.2\times 10^{-7}\ \mathrm{V} = 0.92\ \mu\mathrm{V}.$$

4. The number of ions per s is

$$N_{\text{ion}} = N_{\text{a}} \frac{10^7}{10^7 + 10^8} = 0.091 N_{\text{a}}$$

where N_{a} is the rate of absorbing molecules.

With $\mathrm{d}N_{\text{i}}/\mathrm{d}t = N_{\text{a}} = 10^5\ \text{s}^{-1} \Rightarrow N_{\text{ion}} = 9.1 \times 10^3\ \text{s}^{-1}$.

5. **(a)** The kinetic energy of the molecules impinging per s on the bolometer is

$$\begin{aligned} E_{\text{kin}} &= n \cdot v \cdot \frac{m}{2} v^2 (0.3 \times 0.3) \\ &= 10^8 \times 4 \times 10^4 \times \frac{1}{2} \times 1.66 \times 10^{-27} \times \left(4 \times 10^4\right)^2 \times 9 \times 10^{-6} \cdot 28\ \text{W} \\ &= 1.34 \times 10^{-9}\ \text{W} = P_0. \end{aligned}$$

(b) $\Delta T = P_0 / G = 0.134$ K (dc-temperature rise).

(c) The absorbed laser power is

$$\begin{aligned} \Delta P &= P_0 - P_{\text{t}} = P_0 \left(1 - \mathrm{e}^{-\alpha L}\right) = P_0 \left(1 - \mathrm{e}^{-10^{-9}}\right) \approx P_0 \times 10^{-9} \\ &= 10^{-8}\ \text{mW} = 10^{-11}\ \text{W}. \end{aligned}$$

The rate of absorbed photons is

$$N_{\text{ph}} = \Delta P / h\nu = \Delta P \cdot \lambda / hc = 7.6 \times 10^7\ \text{s}^{-1}.$$

The ac-temperature rise is

$$\Delta T = \frac{\Delta P}{G} = 10^{-11} / 10^{-8}\ \text{K} = 1\ \text{mK}.$$

6. The Zeeman shift for a term with magnetic quantum number M_J $(-J \leq M_J \leq +J)$ is

$$\Delta\nu = \mu \cdot M_J \cdot B / h$$

with the magnetic moment $\mu = 0.5 \mu_{\text{B}}$ we obtain for the frequency shift of the highest Zeeman component $M_J = +J = 2$

$$\begin{aligned} &\Delta\nu = +0.5 \mu_{\text{B}} \cdot J \cdot B / h = 7\ \text{GHz/Tesla} \\ \Rightarrow \quad &B = \frac{10^8 h}{0.5 \times 9.27 \times 10^{-24} \times 2}\ \text{Tesla} = 7.2 \times 10^{-3}\ \text{Tesla}. \end{aligned}$$

The necessary magnetic field for tuning the laser frequency into resonance with the Zeeman component $M'_J = 2 \leftarrow M''_J = 1$ is 7.2 mT.

For the linearly polarized transition $M'_J = 1 \leftarrow M''_J = 1$ the necessary field is twice as high.

For linearly polarized light one observes three Zeeman components when looking perpendicular to $\boldsymbol{B}$. For circular polarization three components appear for σ^+-light and three for σ^--light.

7. **(a)** For a uniform electric field the field strength is

$$E = V/L = 2\ \mathrm{kV/m}.$$

(b) The force acting on the ions is $\boldsymbol{F} = q \cdot \boldsymbol{E}$.

Their acceleration is

$$a = F/m = \frac{2 \times 10^3 \times 1.6 \times 10^{-19}}{40 \times 1.66 \times 10^{-27}}\ \mathrm{m/s^2} = 4.8 \times 10^9\ \mathrm{m/s^2}.$$

Their velocity before the next collision occurs is $v = a \cdot \tau$ where τ is the mean time between two collisions.

The mean free path is $\Lambda = \frac{1}{2} a \tau^2 \Rightarrow \tau = \sqrt{2\Lambda/a} = 6.4 \times 10^{-7}$ s

$$\Rightarrow \quad v_{\max} = \sqrt{2a \cdot \Lambda} = 3.1 \times 10^3\ \mathrm{m/s} = (\Delta v_z)_{\max}.$$

The frequency of the ac-voltage is 1 kHz.

$\Rightarrow$ The period of the electric field is long compared to τ.

$\Rightarrow$ The mean velocity of the ions is $\bar{v} = \frac{1}{2} v_{\max} = 1.6 \times 10^3$ m/s.

(c) The maximum frequency modulation is

$$\Delta\nu = \nu_0 \cdot \Delta v_z / c \approx 10^9\ \mathrm{s^{-1}}.$$

This equals the Doppler width of the absorption lines.

(d) For $\alpha(\nu_0) = 10^{-6}\ \mathrm{cm^{-1}}$ the transmitted power at the line center ν_0 is

$$P_\mathrm{t} = P_0 \cdot \mathrm{e}^{-\alpha z} = P_0 \cdot \mathrm{e}^{-10^{-4}} \approx P_0\left(1 - 10^{-4}\right).$$

At the frequency ν which is 1 GHz away from ν_0 the absorption decreases to

$$\alpha(\nu) = \alpha(\nu_0) \cdot \mathrm{e}^{-\frac{1}{0.36}} = \alpha(\nu_0) \cdot \mathrm{e}^{-2.78} \approx 0.06\alpha(\nu_0).$$

The ac-power modulation is

$$\Delta P_\mathrm{t} = 10\ \mathrm{mW} \times 0.94 \times 10^{-4} = 0.94\ \mu\mathrm{W}.$$

$\Rightarrow$ The detected signal is

$$S = 0.94\ \mathrm{mV}.$$

8. **(a)** According to Eq. (1.6) is

$$\frac{\Delta P}{P_0} = \frac{g_0}{g_0 - \gamma} \cdot \frac{\Delta\gamma}{\gamma + \Delta\gamma}$$

with $\Delta\gamma = 2L \times \alpha = 8 \times 5 \times 10^{-8} = 4 \times 10^{-7}$

$$g_0 = 4 \times 10^{-2}, \qquad \gamma = 2 \times 10^{-2}, \qquad P_0 = 1\ \text{mW}$$

$$\Rightarrow \quad \Delta P = 4 \times 10^{-8}\ \text{W} = 40\ \text{nW}.$$

(b) The intracavity power is

$$P_{\text{int}} = P_0/T = 10^{-3}/\left(5 \times 10^{-3}\right)\ \text{W} = 200\ \text{mW}.$$

The absorbed laser power is

$$P_{\text{abs}} = 2L \cdot \alpha \cdot P_{\text{int}} = 4 \times 10^{-7} \times 0.2\ \text{W} = 8 \times 10^{-8}\ \text{W}.$$

The number of absorbed laser photons per s is

$$n_{\text{a}} = P_{\text{abs}}/(h \cdot \nu) = 2 \times 10^{11}\ \text{s}^{-1}.$$

The number of fluorescence photons is

$$n_{\text{Fl}} = \frac{1}{2} n_{\text{a}} = 1 \times 10^{11}\ \text{s}^{-1}.$$

(c) The fluorescence emitted from the line of the laser beam is best imaged by a cylindrical mirror on one side of the laser beam in the focal line of the mirror which images the line-source into a parallel light beam, directed into the opposite side of the laser beam.

The light beam can be imaged by a spherical lens onto the photo cathode. With this arrangement a collection efficiency of 20 % can be reached.

The number of fluorescence photons impinging onto the cathode is then $0.2 \times 10^{11}\ \text{s}^{-1} = 2 \times 10^{10}\ \text{s}^{-1}$ producing

$$n_{\text{PE}} = 0.15 \times 2 \times 10^{10}\ \text{s}^{-1} = 3 \times 10^{9}\ \text{photoelectrons/s}.$$

(d) The statistical fluctuation of the photoelectron rate is

$$\delta n_{\text{PE}} = \sqrt{n_{\text{PE}}} \approx 5.5 \times 10^{4}\ \text{s}^{-1}.$$

The dark current of the PM at the anode is 10^{-9} A, which gives $10^{-9}/G = 10^{-15}$ A at the cathode.

This corresponds to $n_{\text{D}} = I_\alpha/e = \frac{10^{-15}}{1.6 \times 10^{-19}} = 6.2 \times 10^{3}$ electrons/s.

The shot noise of the signal current is therefore about 9 times larger than the dark current. The signal to noise ratio is $n_{\mathrm{PE}}/\sqrt{n_{\mathrm{PE}}} \approx 5 \times 10^4$.

If the laser power is detected by a photodiode, the signal is $S = (10\ \mathrm{V/W}) \times 10^{-3}\ \mathrm{W} = 10\ \mathrm{mV}$.

The change ΔS due to the change ΔP of the laser power is

$$\Delta S = (10\ \mathrm{V/W}) \times 4 \times 10^{-8}\ \mathrm{W} = 4 \times 10^{-7}\ \mathrm{V}.$$

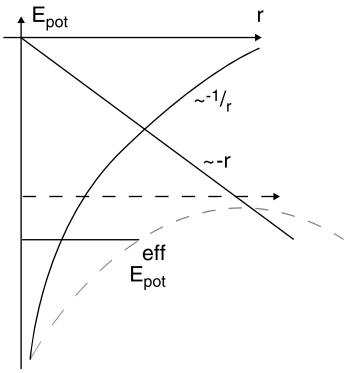
If the laser power can be stabilized within $10^{-3} P_0$ the power fluctuations are 1 μW and the corresponding signal fluctuation $\delta S = 10\ \mu\mathrm{V}$, i.e. about 25 times larger than the signal ΔS. One therefore needs lock-in detection or other special noise-suppressing detection techniques.

9. The total potential energy is the superposition of the Coulomb-potential and the potential $-E_0 \cdot x$ due to the external electric field $\boldsymbol{E} = -E_0 \hat{x}$

$$E_{\mathrm{pot}}^{\mathrm{eff}} = -\frac{Z_{\mathrm{eff}} \cdot \mathrm{e}^2}{4\pi\varepsilon_0 r} - \mathrm{e} \cdot E_0 \cdot x.$$

With $x = r \cdot \cos\vartheta$ we obtain for $\vartheta = 0$

$$E_{\mathrm{pot}}^{\mathrm{eff}} = -\frac{Z_{\mathrm{eff}} \cdot \mathrm{e}^2}{4\pi\varepsilon_0 r} - \mathrm{e} \cdot E_0 \cdot r.$$



This function has a maximum at $r = r_{\mathrm{m}}$ for $\mathrm{d}E_{\mathrm{pot}}^{\mathrm{eff}}/\mathrm{d}r = 0$

$$\Rightarrow \quad \frac{Z_{\mathrm{eff}} \cdot \mathrm{e}^2}{4\pi\varepsilon_0 r_{\mathrm{m}}^2} - \mathrm{e} \cdot E_0 = 0$$

$$\Rightarrow \quad r_{\mathrm{m}} = \left(\frac{Z_{\mathrm{eff}} \cdot \mathrm{e}}{4\pi\varepsilon_0 E_0}\right)^{1/2}$$

$$\Rightarrow \quad E_{\mathrm{pot}}^{\mathrm{eff}}(r_{\mathrm{m}}) = \sqrt{\frac{Z_{\mathrm{eff}} \cdot \mathrm{e}^3 E_0}{\pi\varepsilon_0}}.$$

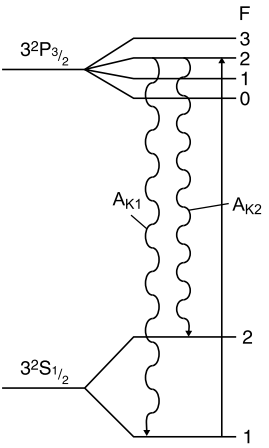
The ionization potential $IP = E_1 - E_{\mathrm{pot}}(\infty)$ is lowered to

$$IP^{\mathrm{eff}} = IP - \sqrt{\frac{Z_{\mathrm{eff}} \cdot \mathrm{e}^3 E_0}{\pi\varepsilon_0}}.$$

Chapter 2

1. **(a)** With the lifetime $\tau_K = 16\ \mathrm{ns}$ of the upper level with $F' = 2$ the total transition probability is

$$A_K = A_{K1} + A_{K2} = \frac{1}{\tau_K} = 6.3 \times 10^7 \text{ s}^{-1}.$$



The intensity ratio of the two hf-components is

$$\frac{I(F' = 2 \to F_1'' = 1)}{I(F' = 2 \to F_2'' = 2)} = \frac{2F_1'' + 1}{2F_2'' + 1} = \frac{3}{5}.$$

This gives for the Einstein coefficients

$$A_{K1} = \frac{3}{8} A_K; \qquad A_{K2} = \frac{5}{8} A_K.$$

The transit time t_T of Na-atoms through the laser beam with $d = 0.01$ cm is

$$t_\mathrm{T} = d/\bar{v} = \frac{10^{-2}}{5 \times 10^4} \text{ s} = 2 \times 10^{-7} \text{ s}.$$

The total relaxation rate into the lower level $F'' = 1$ is

$$R\big(F'' = 1\big) = N \cdot A + n_K\big(F' = 2\big) \cdot A \cdot d \cdot A_{K1}$$

where $N \cdot A = n(F'' = 1) \cdot A \cdot \bar{v}$ is the flux of atoms in level $F'' = 1$ through the focal area $A = 0.2 \times 0.01$ cm^2, n [cm^{-3}] is the atomic density and $d = 0.01$ cm the pathlength through the focussed laser beam.

According to (2.20) the saturation intensity is then

$$\begin{aligned} I_\mathrm{S} &= 2\sqrt{2} \cdot h\nu(A_{K1} + 1/t_\mathrm{T})/\lambda^2 \quad \text{with } t_\mathrm{T} = d/\bar{v} \\ &= 2.8hc(A_{K1} + 1/t_\mathrm{T})/\lambda^3 \\ &= 77 \text{ W/m}^2. \end{aligned}$$

The necessary laser power is

$$P = I \cdot A = 15.4 \text{ μW}.$$

(b) The Doppler width is here larger than the hfs-splittings of the upper state. The pressure broadening is 250 MHz. The lower hfs-level $F'' = 1$ can be populated from the upper levels with $F' = 0, 1, 2$ and by collisional transfer from these levels and from $F'' = 2$.

The total refilling rate of level $F'' = 1$ is given by the sum of radiative transfer

$$R^\mathrm{rad} = N_2' A_{21} + N_1' A_{11} + N_0' A_{01} = (5A_{21} + 3A_{11} + A_{01})N'/9 \approx A_k \cdot N_K$$

and the collisional transfer rate.

We have assumed that all hfs levels are equally populated apart from their statistical weights $(2F + 1)$, because the collision broadening is larger than the natural linewidth and the hfs-splittings. The collisional refilling probability is $R_{\text{coll}} = 2\pi \times 2.5 \times 10^8\ \text{s}^{-1} \approx 1.5 \times 10^9\ \text{s}^{-1}$.

This gives for the saturation intensity

$$I_{\text{S}} = \frac{2.8hc}{\lambda^3}(A_K + R_{\text{coll}}) = 4.3 \times 10^3\ \text{W/m}^2$$

and a laser power

$$P = I \cdot A = 8.6 \times 10^{-4}\ \text{W} = 0.86\ \text{mW}.$$

2. The transmitted power is

$$P_{\text{t}} = P_0 \cdot \text{e}^{-N_i \sigma x}.$$

From $p = 10\ \text{mbar} = 10^3\ \text{Pa} \Rightarrow n = p/kT = 2.4 \times 10^{23}\ \text{m}^{-3}$.

The density of absorbing atoms is

$$n_i = 2.4 \times 10^{17}\ \text{cm}^{-3}$$

$$\Rightarrow \quad P_{\text{t}} = P_0 \cdot \text{e}^{-10^{-3}} \quad \text{for } x = 1\ \text{cm}$$

$$\Rightarrow \quad \frac{\Delta P}{P_0} = \frac{(P_{\text{t}} - P_0)}{P_0} \approx 10^{-3}.$$

The number of absorbed photons is

$$n_{\text{a}} = \frac{1}{3}\frac{\Delta P \cdot \Delta T}{h\nu} = 1.5 \times 10^{10}\ \text{photons/cm}^3.$$

The factor $1/3$ takes into account that the laser bandwidth is three times the absorption linewidth.

$\Rightarrow$ The fraction of excited atoms is than

$$\frac{n_{\text{a}}}{n_i} = \frac{1.5 \times 10^{10}}{2.4 \times 10^{17}} = 6.3 \times 10^{-8}.$$

3. Because of the Kramers–Kronig-relation the change Δn of the refractive index is related to the change $\Delta\alpha$ of the absorption coefficient by

$$\Delta n = \frac{2c}{\omega_0}\Delta\alpha.$$

The phase shift between the σ^+ and σ^- component is

$$\Delta\phi = \frac{\omega \cdot L}{c}\Delta n = 2L \cdot \Delta\alpha = 2 \times 10^{-2}\alpha_0 \cdot L$$

$$\Rightarrow \quad \Delta\phi = 2 \times 10^{-2} \times 5 \times 10^{-2} = 10^{-3}.$$

The angle of the polarization plane has changed by

$$\Delta\varphi = \frac{1}{2}\Delta\phi = \frac{1}{2} \times 10^{-3} \text{ rad} \mathrel{\hat{=}} 0.03°.$$

4. The number of detected fluorescence photons per s is

$$n_{\text{Fl}} = 0.05 \cdot 0.2 \cdot n_{\text{a}}/2$$

where n_{a} is the rate of absorbed laser photons.

The rate of incident laser photons is

$$n_{\text{ph}} = (I/h\nu) \cdot A = 10^{-1}/\left(6.6 \times 10^{-34} \times 5 \times 10^{14}\right) = 3 \times 10^{12} \text{ s}^{-1}$$

where $A = \pi\omega_0^2$ is the cross section of the laser beam.

The absorption probability per atom is

$$P_{\text{if}} = \sigma \cdot n_{\text{ph}}/A = a \cdot I \cdot n_{\text{ph}}/A = a \cdot h\nu n_{\text{ph}}^2/A^2 = 6 \times 10^{-4}.$$

This gives the number of absorbed photons $= \frac{1}{2}$ number of excited atoms

$$\begin{aligned} n_{\text{a}} &= n \cdot A \cdot L \cdot P_{\text{if}} = 10^{12} \times \pi \times 10^{-4} \times 1 \times 6 \times 10^{-4} \\ &= 1.9 \times 10^5 \text{ s}^{-1} \end{aligned}$$

$$\Rightarrow \quad n_{\text{Fl}} = 10^{-2} \times \frac{1}{2} \times 1.9 \times 10^5 = 9.5 \times 10^2 \text{ s}^{-1}.$$

With a quantum efficiency of 20 % of the photo cathode one obtains a counting rate of 1.9×10^2 counts/s.

5. The saturation signal is proportional to $\alpha^0 - \alpha_{\text{S}}$, where α is the absorption coefficient.

$$\left(\alpha^0 - \alpha_{\text{S}}\right) \propto S \cdot \alpha^0.$$

For the transition $(F'' = 1 \rightarrow F' = 1)$ the saturation parameter is $S_1 = 2$. The transition probability ratio R for the two transitions $(F'' = 1 \rightarrow F_1' = 1)$ and $(F'' = 1 \rightarrow F_2' = 2)$ is

$$R = \frac{2F_1' + 1}{2F_2' + 1} = \frac{3}{5}.$$

Therefore the saturation parameter $S_2 = \frac{5}{3} \cdot S_1 = 3.3$.

The saturation signal amplitudes A are

$$\left(\Delta N^0 - \Delta N\right) \cdot I \propto \Delta N_0 \cdot S \cdot I.$$

For the cross-over signal only $I/2$ is acting on each transition. Therefore the saturation parameters are $S_1/2$ and $S_2/2$

$$A_{\text{co}} = \frac{\Delta N_0}{2}(S_1 + S_2) \cdot I/2 = \frac{\Delta N_0}{4}(2 + 3.3) = \frac{5.3}{4}\Delta N_0 I$$

while the saturation signals are

$$A_1 = 2\Delta N_0 I \quad \text{and} \quad A_2 = 3.3\Delta N_0 I$$

$$A_{\text{co}} = \frac{1}{4}(A_1 + A_2).$$

6. The linewidth γ is mainly determined by the transit time t_{T} of the H atoms through the laser beam

$$t_{\text{T}} = d/\bar{v} = \frac{10^{-3}}{10^3}\ \text{s} = 10^{-6}\ \text{s} \quad \Rightarrow \quad \gamma = \frac{1}{t_{\text{T}}} = 10^6\ \text{s}^{-1}.$$

From $h\nu = \frac{1}{2}[E(2S_{1/2}) - E(1S_{1/2})] \Rightarrow \nu = 1.23 \times 10^{15}\ \text{s}^{-1}$

$$\Rightarrow \quad P_{\text{if}} = \sigma_0^2 \frac{I^2}{(\gamma \cdot h\nu)^2} = 1.5 \times 10^{-6}$$

$$\Rightarrow \quad 1.5 \times 10^{-6} \quad \text{of all atoms are excited into the } 2\,^2S_{1/2} \text{ level.}$$

Chapter 3

1. The flux density of incident photons, focussed to the area A from a laser with output power P is

$$N_{\text{ph}} = \frac{P}{h\nu \cdot A} = 2.5 \times 10^{21}\ \text{photons}/(\text{s}\,\text{cm}^2).$$

The rate of scattered photons at a molecular density N_{i} in the volume V is

$$N_{\text{sc}} = N_{\text{ph}} \cdot N_{\text{i}} \cdot V \cdot \sigma$$

$$= 1.25 \times 10^{-11}\ N_{\text{i}}.$$

The rate of photoelectrons is

$$N_{\text{PE}} = \delta \cdot \eta \cdot N_{\text{sc}} = 0.1 \times 0.25 \times 1.25 \times 10^{-11}\ N_{\text{i}}/\text{s}$$

$$= 3.1 \times 10^{-13}\ N_{\text{i}}/\text{s}.$$

This number should be larger than 30

$$\Rightarrow \quad N_{\text{i}} > \frac{30}{3.1 \times 10^{-13}}\ \text{cm}^{-3} = 9.7 \times 10^{13}\ \text{cm}^{-3}.$$

2. The $3N - 6 = 3$ normal modes of H_2O are: The symmetric stretch ν_1, the bending vibration ν_2 and the asymmetric stretch ν_3

Problems & Solutions on Laser Spectroscopy

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Based on Demtroder's

Laser Spectroscopy,

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Chapter 1.1

Problems

Problems for Dem. Vol. 2

Problem Set — §1.1 Advantages of Lasers in Spectroscopy

A. Numerical (5)

N1. Minimum detectable number density from NEP

A single-mode laser beam (power $P_0 = 25\,\mathrm{mW}$) probes an absorption cell of length $L = 8\,\mathrm{m}$. The detection chain has effective proportionality $a = 0.85$ and the detector's noise-equivalent power is $NEP = 2.0\,\mathrm{pW}$ (in the measurement bandwidth). The on-resonance absorption cross section of the transition is $\sigma_{ik} = 2.5 \times 10^{-16}\,\mathrm{cm}^2$.

Assuming small absorption, estimate the **minimum detectable number density** $N_i^{\min}$.

Solution (step-by-step)

1. Sensitivity condition (from $S = a\Delta P > a\,P_0 N_i \sigma_{ik} L \geq NEP$):

$$N_i^{\min} = \frac{NEP}{a\,P_0\,\sigma_{ik}\,L}.$$

2. Put all quantities in consistent units. Use $L = 8\,\mathrm{m} = 800\,\mathrm{cm}$; $P_0 = 25 \times 10^{-3}\,\mathrm{W}$.

3. Insert numbers:

$$N_i^{\min} = \frac{2.0 \times 10^{-12}}{0.85 \times 25 \times 10^{-3} \times 2.5 \times 10^{-16} \times 800} \approx 4.71 \times 10^{2}\,\mathrm{cm}^{-3}.$$

Answer: $\boxed{N_i^{\min} \approx 4.7 \times 10^{2}\ \mathrm{cm}^{-3}}$.

N2. Laser vs. conventional: $\alpha_{\min}$ and improvement factor

With intensity-stabilized detection, assume the minimum measurable relative absorption is $\Delta P/P \approx 10^{-6}$. Use

$$\alpha_{\min} = \frac{10^{-6}}{L}\,\frac{\Delta\omega}{\delta\omega}.$$

Case (A) “conventional”: $L = 20\ \text{cm}$, $\Delta\omega/\delta\omega = 10$.

Case (B) “single-mode laser”: $L = 20\ \text{m}$, $\Delta\omega/\delta\omega = 0.3$.

Compute $\alpha_{\min}$ for both and the improvement factor $F = \alpha_{\min}^{(A)}/\alpha_{\min}^{(B)}$.

Solution

- Case A:

$$\alpha_{\min}^{(A)} = \frac{10^{-6}}{20} \times 10 = 5.0 \times 10^{-7}\ \text{cm}^{-1}.$$

- Case B: $L = 20\ \text{m} = 2000\ \text{cm}$,

$$\alpha_{\min}^{(B)} = \frac{10^{-6}}{2000} \times 0.3 = 1.5 \times 10^{-10}\ \text{cm}^{-1}.$$

- Improvement:

$$F = \frac{5.0 \times 10^{-7}}{1.5 \times 10^{-10}} \approx 3.33 \times 10^{3}.$$

Answer: $\boxed{\alpha_{\min}^{(A)} = 5.0 \times 10^{-7}\ \text{cm}^{-1},\ \alpha_{\min}^{(B)} = 1.5 \times 10^{-10}\ \text{cm}^{-1},\ F \approx 3.3 \times 10^{3}}$.

N3. Fabry–Perot interferometer markers

A plane-parallel FPI of mirror spacing $d = 0.75\ \text{m}$ is used as a frequency ruler.

(a) Compute the free spectral range (FSR) $\Delta\nu_p = c/(2d)$.

(b) At $\lambda = 600\ \text{nm}$, what is the wavelength spacing $\Delta\lambda$ of successive transmission peaks?

Solution

(a)

$$\Delta\nu_p = \frac{c}{2d} = \frac{3.0 \times 10^{8}}{2 \times 0.75} = 2.0 \times 10^{8}\ \text{Hz} = 200\ \text{MHz}.$$

(b) Using $\nu = c/\lambda$ and $d\nu = (c/\lambda^2)\, d\lambda \Rightarrow \Delta\lambda = (\lambda^2/c)\, \Delta\nu$:

$$\Delta\lambda = \frac{(600 \times 10^{-9})^2}{3.0 \times 10^8} \times 2.0 \times 10^8 = 2.4 \times 10^{-13}\ \text{m} = 2.4 \times 10^{-4}\ \text{nm}.$$

Answer: $\boxed{\Delta\nu_p = 200\ \text{MHz},\ \Delta\lambda \approx 2.4 \times 10^{-4}\ \text{nm}}$.

(For a semiconfocal FPI, $FSR = c/(8d) = 50\ \text{MHz} \Rightarrow \Delta\lambda \approx 6.0 \times 10^{-5}\ \text{nm}$ at 600 nm.)

N4. Resolution-dependent signal size (rectangular line)

Assume the absorption line has a **rectangular** profile of width $\delta\omega$ and height α_0 (zero elsewhere). You measure with resolution bandwidth $\Delta\omega$ and pathlength Δx.

Given $\alpha_0 = 2.0 \times 10^{-8}\ \text{cm}^{-1},\ \delta\omega = 2\pi \times 1.0\ \text{GHz},\ \Delta x = 5\ \text{cm}$:

(a) For coarse resolution $\Delta\omega = 2\pi \times 10\ \text{GHz}$, find $\Delta P/P$.

(b) For fine resolution $\Delta\omega \ll \delta\omega$ (e.g. $\Delta\omega = 2\pi \times 0.1\ \text{GHz}$), what is $\Delta P/P$ at line center?

Solution

When $\Delta\omega > \delta\omega$:

$$\frac{\Delta P}{P} = \frac{\Delta x}{\Delta\omega} \int \alpha(\omega)\, d\omega = \frac{\Delta x\, \alpha_0\, \delta\omega}{\Delta\omega}.$$

(a) Ratio $\delta\omega/\Delta\omega = 1/10$. Thus

$$\frac{\Delta P}{P} = 5\ \text{cm} \times 2.0 \times 10^{-8}\ \text{cm}^{-1} \times \frac{1}{10} = 1.0 \times 10^{-8}.$$

(b) If $\Delta\omega \ll \delta\omega$, at line center:

$$\frac{\Delta P}{P} = \Delta x\, \alpha(\omega_0) = \Delta x\, \alpha_0 = 5 \times 2 \times 10^{-8} = 1.0 \times 10^{-7}.$$

Answer: $\boxed{\text{(coarse)}\ \Delta P/P = 1.0 \times 10^{-8};\quad \text{(fine, on line)}\ \Delta P/P = 1.0 \times 10^{-7}}$.

N5. Determining FPI spacing from a scan

A laser is scanned linearly over $1.50\ \mathrm{GHz}$. The FPI transmission signal shows **21** equally spaced peaks across the scan range. Assuming a plane-parallel FPI, determine the mirror spacing d.

Solution

There are 21 peaks → 20 equal intervals.

$$\Delta\nu_p = \frac{1.50\ \mathrm{GHz}}{20} = 75\ \mathrm{MHz}.$$

Plane FPI FSR: $\Delta\nu_p = c/(2d) \Rightarrow d = c/(2\Delta\nu_p)$:

$$d = \frac{3.0 \times 10^8}{2 \times 75 \times 10^6} = 2.0\ \mathrm{m}.$$

Answer: $\boxed{d = 2.0\ \mathrm{m}}$.

B. Analytical / Symbolic (5)

A1. Small-absorption approximation from Beer–Lambert

Starting from $P_T = P_0 e^{-\alpha L}$, derive (to first order in $\alpha L \ll 1$):

$$P_T \approx P_0(1 - \alpha L), \quad \Delta P = P_0 - P_T \approx P_0\,\alpha L.$$

Solution

Expand $e^{-\alpha L} \approx 1 - \alpha L + 1/2\,(\alpha L)^2 - \cdots$.

Neglect $\mathcal{O}((\alpha L)^2)$: $P_T \approx P_0(1 - \alpha L)$.

Thus $\Delta P = P_0 - P_T \approx P_0 \alpha L$.

Answer: Derived as above.

A2. Sensitivity limit for $\alpha_{\min}$ from NEP

Given measured signal $S = a\,\Delta P = a\,P_0\,\alpha L$ (small absorption), and the detection threshold $S \geq NEP$, obtain:

$$\boxed{\alpha_{\min} = \frac{NEP}{a\,P_0\,L}}.$$

Solution

Set $a\,P_0\,\alpha_{\min} L = NEP \Rightarrow \alpha_{\min} = \frac{NEP}{a\,P_0\,L}$.

Answer: As boxed.

A3. Minimum detectable density $N_i^{\min}$

With $\alpha = N_i\,\sigma_{ik}$, combine with A2 to show

$$\boxed{N_i^{\min} = \frac{NEP}{a\,P_0\,\sigma_{ik}\,L}}.$$

Solution

Insert $\alpha = N_i\sigma_{ik}$ into $aP_0\alpha L = NEP$. Solve for N_i.

Answer: As boxed.

A4. Resolution-dependent attenuation formula

Assume $P(\omega)$ is nearly constant over the resolution bandwidth $\Delta\omega$ centered at ω_0. Show

$$\frac{\Delta P}{P} = \begin{cases} \dfrac{\Delta x}{\Delta\omega}\displaystyle\int_{\omega_0-\Delta\omega/2}^{\omega_0+\Delta\omega/2} \alpha(\omega)\,d\omega \simeq \overline{\alpha}\,\Delta x\,\dfrac{\delta\omega}{\Delta\omega}, & \Delta\omega > \delta\omega, \\ \alpha(\omega_0)\,\Delta x, & \Delta\omega \ll \delta\omega. \end{cases}$$

Solution

Starting from the definition in the text for small absorption, average the attenuation over $\Delta\omega$:

$$\frac{\Delta P}{P} = \frac{\Delta x}{\Delta\omega}\int \alpha(\omega)\,d\omega \quad \left(\text{if } P(\omega) \approx \overline{P}\right).$$

If $\Delta\omega > \delta\omega$, only the line contributes; approximate $\int \alpha(\omega)d\omega \approx \overline{\alpha}\,\delta\omega$.

If $\Delta\omega \ll \delta\omega$, the line is locally flat: $\alpha(\omega) \approx \alpha(\omega_0)$.

Answer: As stated.

A5. Impact of source power fluctuations on α uncertainty

If fractional source fluctuations are $\delta P/P$, what **apparent absorption uncertainty** $\delta\alpha$ do they cause? Give expressions for the two regimes.

Solution

Measured $\Delta P/P$ includes true absorption plus noise. The noise term $\sim \delta P/P$ maps to an equivalent $\delta\alpha$ via the signal formulas:

- For $\Delta\omega \ll \delta\omega$: $\Delta P/P \approx \alpha\,\Delta x \Rightarrow \delta\alpha \approx \frac{\delta P/P}{\Delta x}$.
- For $\Delta\omega > \delta\omega$: $\Delta P/P \approx \overline{\alpha}\Delta x\,\frac{\delta\omega}{\Delta\omega} \Rightarrow \delta\alpha \approx \frac{\delta P/P}{\Delta x}\,\frac{\Delta\omega}{\delta\omega}$.
- **Answer:** $\boxed{\delta\alpha \approx (\delta P/P)/\Delta x}$ (narrowband); $\boxed{\delta\alpha \approx (\delta P/P)\,(\Delta\omega/\delta\omega)/\Delta x}$ (coarse resolution).

C. Qualitative / Descriptive (5)

Q1. Why no monochromator with lasers?

Solution (steps)

1. A tunable single-mode laser already provides a narrow, selectable frequency.
2. You directly measure transmission vs. laser frequency; no dispersive element is needed to **select** the wavelength.
3. Spectral resolution is then limited by the **molecular line** (Doppler or pressure broadened) and the **laser linewidth**, not by spectrometer resolving power.
4. **Answer:** Lasers supply the spectral selectivity; resolution is set by laser and transition linewidths, not a monochromator.

Q2. Long pathlengths: benefits and trade-offs

Solution (steps)

1. Benefit: $\Delta P/P \sim \alpha L \rightarrow$ increasing L boosts signal linearly, improving sensitivity to tiny α.
2. Implementation: Use multipass cells (Herriott/White), good beam collimation, Brewster windows to suppress stray reflections.
3. Trade-offs: At higher pressure, pressure broadening grows; but higher sensitivity lets you **lower** gas pressure to reduce pressure broadening.
4. Practical limits: Mirror losses, alignment stability, and speckle/etalon effects can limit effective L.
5. **Answer:** Long L greatly improves sensitivity and can enable **lower-pressure** operation to reduce broadening; alignment and optical losses must be managed.

Q3. Using an FPI for frequency calibration

Solution (steps)

1. A small fraction of the laser is sent to an FPI of spacing d.
2. As the laser is scanned, the detector records transmission peaks whenever $\nu_L = m\,c/(2d)$.
3. The constant FSR $\Delta\nu_p = c/(2d)$ provides a **ruler**; counting peaks/intervals calibrates the scan axis.
4. This lets you measure **separations of absorption lines** with MHz-level accuracy.
5. **Answer:** The FPI's evenly spaced transmission maxima serve as precise frequency markers to calibrate the laser scan.

Q4. Key noise sources and how lasers help

Solution (steps)

1. **Source intensity noise**: lasers can be power-stabilized (servoing pump/attenuator) to $\delta P/P \lesssim 10^{-4}$.
2. **Detector noise**: with lasers' high spectral power density, detector noise often becomes negligible.
3. **Beam pointing**: small detector areas + thermal lensing can convert pointing jitter into amplitude noise; use spatial filtering and large-area/ integrating detectors.
4. **Laser frequency noise**: if laser linewidth $<$ absorption linewidth, frequency jitter maps to amplitude variations off line center; lock the laser to the line or use modulation schemes (FM spectroscopy).
5. **Density fluctuations**: usually minor in stable cells; average or control flow/temperature.
6. **Answer:** Lasers allow strong mitigation (power and frequency stabilization, spatial conditioning), pushing the sensitivity to very small absorptions.

Q5. When are multimode lasers OK?

Solution (steps)

1. If the application (e.g., optical pumping, broadband fluorescence excitation) does **not** require resolving closely spaced transitions.
2. If the **mode sweep/jitter** remains small compared to the **absorption linewidth** so that line-center averaging is acceptable.
3. When higher total power over a modest bandwidth is beneficial for population transfer or detection.
4. **Answer:** Multimode lasers are acceptable when resolution demands are modest and frequency jitter is small vs. the line, or when broad, high-power excitation is desired.

(Optional) Teaching Notes & Quick Uses

- Use **N2** in class to quantify the dramatic sensitivity gain from single-mode lasers + long L.

- **N3/N5** make excellent lab-calibration questions for FPIs.
- Pair **A4** with **N4** to connect the math to measurable signal scaling.
- **Q4** is a checklist for lab design and oral exams.

Chapter 1.2

Problems

Problem Set — §1.2 High-Sensitivity Methods of Absorption Spectroscopy

A) Numerical (5)

N1. Multipass cell transmission

A multipass cell uses two spherical mirrors of reflectivity $R = 0.995$. The beam makes $q = 120$ roundtrips through an absorption cell of length $L = 30$ cm containing a weakly absorbing gas with coefficient $\alpha = 2.0 \times 10^{-6}$ cm^{-1}.

Using

$$I_T = I_0 \exp[-2q(1-R) - 2q\,\alpha L],$$

find I_T/I_0.

Solution

1. Mirror loss term: $1 - R = 0.005 \Rightarrow 2q(1-R) = 2 \cdot 120 \cdot 0.005 = 1.2$.
2. Absorption term: $\alpha L = 2.0 \times 10^{-6} \cdot 30 = 6.0 \times 10^{-5}$.
3. $\Rightarrow 2q\alpha L = 2 \cdot 120 \cdot 6.0 \times 10^{-5} = 240 \cdot 6.0 \times 10^{-5} = 1.44 \times 10^{-2}$.
4. Total exponent: $-1.2 - 0.0144 = -1.2144$.
5. $I_T/I_0 = e^{-1.2144} \approx 0.30 \times 0.986 \approx 0.297$.

Answer: $\boxed{I_T/I_0 \approx 0.297}$.

N2. External enhancement cavity: absorbed power & SNR

A single-mode laser of power $P_0 = 10$ mW is coupled into an external passive cavity with mirror reflectivity $R = 0.990$. A sample with $\alpha = 5.0 \times 10^{-7}$ cm^{-1} fills $L = 50$ cm inside the cavity. The detector chain has $NEP = 5$ pW in the measurement bandwidth.

Assuming small absorption, compute (i) the intracavity power P_{int}, (ii) the absorbed power $\Delta P \approx \alpha L\, P_{\text{int}}$, and (iii) the SNR $\Delta P / NEP$.

Solution

(i) $P_{\text{int}} = \frac{P_0}{1-R} = \frac{0.010}{0.01} = 1.0$ W.

(ii) $\alpha L = 5.0 \times 10^{-7} \cdot 50 = 2.5 \times 10^{-5} \Rightarrow \Delta P = 2.5 \times 10^{-5} \cdot 1.0 = 25\ \mu$W.

(iii) $SNR = \frac{25 \times 10^{-6}}{5 \times 10^{-12}} = 5.0 \times 10^{6}$.

Answer: $P_{\text{int}} = 1.0$ W, $\Delta P = 25\ \mu$W, $SNR \approx 5 \times 10^{6}$.

N3. Frequency modulation via cavity-length dither

A diode laser with external cavity length $d = 10$ cm at $\lambda = 780$ nm is frequency-modulated by dithering d. The mode index is $q \approx 2d/\lambda$.

What mirror spacing change Δd is required to span a Doppler width $\Delta \nu_D = 1.2$ GHz? Use

$$\nu = \frac{qc}{2d}, \qquad \Delta \nu = \frac{qc}{2d^2}\,\Delta d \;\Rightarrow\; \Delta d = \frac{2d^2}{qc}\,\Delta \nu.$$

Solution

1. $q \approx \frac{2d}{\lambda} = \frac{0.20}{7.80 \times 10^{-7}} \approx 2.564 \times 10^{5}$.
2. $2d^2 = 2(0.10)^2 = 0.02\ \text{m}^2$.
3. $qc \approx 2.564 \times 10^{5} \cdot 3.0 \times 10^{8} = 7.692 \times 10^{13}$.
4. $\Delta d = \frac{0.02}{7.692 \times 10^{13}} \cdot 1.2 \times 10^{9} = 3.12 \times 10^{-7}\ \text{m} = 0.312\ \mu$m.

Answer: $\boxed{\Delta d \approx 0.31\ \mu\text{m}}$.

N4. Phase modulation: modulation index and sideband power

A $LiTaO_3$ phase modulator (optical thickness $L = 1.0$ cm, refractive index $n_0 = 1.6$) at $\lambda = 532$ nm is driven so that $n(t) = n_0[1 + b\sin(\Omega t)]$ with $b = 1.1 \times 10^{-6}$.

Compute the modulation index $\beta = \Delta\phi_m$ and estimate the fraction of optical power in each first-order sideband using the small-signal relation $J_1(\beta) \approx \beta/2$ (sideband power $\approx J_1^2$).

Solution

$$\beta = \frac{2\pi}{\lambda} n_0 L\, b = \frac{2\pi}{5.32 \times 10^{-7}} \cdot (1.6 \cdot 0.01) \cdot 1.1 \times 10^{-6}.$$

$\frac{2\pi}{\lambda} \approx 1.18 \times 10^7$ rad/m.

$n_0 Lb = 1.6 \times 0.01 \times 1.1 \times 10^{-6} = 1.76 \times 10^{-8}$.

$\Rightarrow \beta \approx 1.18 \times 10^7 \cdot 1.76 \times 10^{-8} = 0.2077.$

Small-signal: $J_1 \approx \beta/2 \approx 0.104 \Rightarrow$ sideband power $\approx 0.104^2 \approx 0.0108$ (≈1.1%) in each first order.

Answer: $\beta \approx 0.208$; each first-order sideband carries $\sim 1.1\%$ of the power.

N5. Time-resolved ICLAS: effective path and $\alpha_{\min}$

In time-resolved intracavity laser absorption (ICLAS), the signal is gated at $t = 2.0$ ms after turn-on. A 0.5% dip is the smallest reliably detectable change. Estimate the effective path $L_{\text{eff}} = ct$ and the minimum detectable $\alpha_{\min} \approx 0.005/L_{\text{eff}}$ (in cm^{-1}). Compare to a single-pass 10 m cell with the same 0.5% limit.

Solution

1. $L_{\text{eff}} = 3.0 \times 10^8 \cdot 2.0 \times 10^{-3} = 6.0 \times 10^5$ m $= 6.0 \times 10^7$ cm.
2. $\alpha_{\min} = 0.005/6.0 \times 10^7 = 8.33 \times 10^{-11}\ \text{cm}^{-1}$.
3. Single-pass 10 m $= 10^3$ cm $\Rightarrow \alpha_{\min}^{(1\text{pass})} = 0.005/10^3 = 5.0 \times 10^{-6}\ \text{cm}^{-1}$.
4. Improvement factor $\approx \frac{5.0\times10^{-6}}{8.33\times10^{-11}} \approx 6.0 \times 10^4$.

Answer: $L_{\text{eff}} = 600$ km, $\alpha_{\min} \approx 8.3 \times 10^{-11}\ \text{cm}^{-1}$; $\sim 6 \times 10^4\times$ more sensitive than a 10 m single pass.

B) Analytical / Symbolic (5)

A1. Effective path length in a multipass cell

Show that the total absorption in a multipass cell that makes q roundtrips through a cell of length L behaves like a single pass with **effective path** $L_{\text{eff}} = 2qL$ (ignoring mirror losses in the absorption term).

Solution

Each roundtrip contributes two traversals of length L, so the total geometric path through the absorber is $2qL$. For $\alpha L \ll 1$,

$$I_T = I_0\, e^{-2q(1-R)}\, e^{-2q\alpha L} = I_0\, e^{-2q(1-R)}\, e^{-\alpha L_{\text{eff}}}.$$

Thus the absorption factor equals that of a single pass of length $L_{\text{eff}} = 2qL$.

Answer: $L_{\text{eff}} = 2qL$ (for the absorption term).

A2. Intracavity power build-up from a geometric series

Derive $P_{\text{int}} = \frac{P_0}{1-R}$ for a critically coupled single-ended cavity with mirror reflectivity R and negligible other losses, assuming steady-state continuous injection P_0 and perfect mode matching.

Solution

Each roundtrip multiplies the intracavity field by $\sqrt{R}$ (power by R). The injected field adds coherently; at resonance the circulating power sums as a geometric series:

$$P_{\text{int}} = P_0\,(1 + R + R^2 + \cdots) = \frac{P_0}{1-R}.$$

(Here "P_0" denotes the coupled power into the resonant mode.)

Answer: $P_{\text{int}} = P_0/(1-R)$.

A3. Frequency-modulation (FM) detection gives derivatives

Starting from $P_T(\omega) = P_0 e^{-\alpha(\omega)x}$ with $\alpha x \ll 1 \Rightarrow P_T \approx P_0[1 - \alpha(\omega)x]$, show that a small sinusoidal frequency modulation $\omega_L(t) = \omega_0 + a\sin\Omega t$ produces a lock-in signal at Ω proportional to $\frac{d\alpha}{d\omega}$ evaluated at ω_0.

Solution

1. $P_T\big(\omega_L(t)\big) \approx P_0\{1 - x[\alpha(\omega_0) + a\sin\Omega t\, \alpha'(\omega_0) + \cdots]\}$.
2. AC term at Ω: $-P_0 x\, a\, \alpha'(\omega_0)\sin\Omega t$.
3. Normalizing by P_0 and reading the lock-in component at Ω yields

$$S(\Omega) \propto -a\, x\, \frac{d\alpha}{d\omega}|_{\omega_0}.$$

Answer: $S(\Omega) \propto -a\, x\, \alpha'(\omega_0)$.

A4. Optimal FM frequency scale

Show that for derivative spectroscopy on an absorption line of HWHM γ (FWHM $= 2\gamma$), choosing the FM offset (or effective separation of carrier/sideband interaction) on the order of the linewidth maximizes slope sensitivity. Give a scaling argument.

Solution

The FM signal at Ω compares $\alpha(\omega_0 \pm a)$. For small a, $S \propto a\, \alpha'(\omega_0)$, but $|\alpha'|$ itself peaks when the sampling points straddle the line's inflection region, i.e., at detunings comparable to γ (e.g., for a Lorentzian, $|\alpha'|$ peaks at $|\omega - \omega_0| = \gamma/\sqrt{3}$). Hence, choosing the modulation scale $a \sim \gamma$ (or Ω comparable to the linewidth in phase-modulation implementations) maximizes signal per unit drive.

Answer: Use $a \sim \gamma$ (or Ω comparable to the linewidth) for near-optimal slope sensitivity.

A5. Intracavity absorption enhancement Q

Given steady-state single-mode output

$$P = P_s \frac{g_0 - \gamma}{\gamma}, \quad P_\alpha = P_s \frac{g_0 - \gamma - \Delta\gamma}{\gamma + \Delta\gamma},$$

show that for $\Delta\gamma \ll \gamma$,

$$\frac{\Delta P}{P} \simeq \frac{g_0}{g_0 - \gamma} \frac{\Delta\gamma}{g_0 - \gamma} = \frac{g_0}{\gamma(g_0 - \gamma)} \Delta\gamma \equiv Q\, \Delta\gamma.$$

Then (i) derive $Q \simeq 1/\gamma$ far above threshold ($g_0 \gg \gamma$), and (ii) show that if $\gamma \approx T_2$ (output coupler transmission dominates), $Q \approx 1/T_2 = q$.

Solution

Linearizing (given) yields $Q = \frac{g_0}{\gamma(g_0 - \gamma)}$.

(i) If $g_0 \gg \gamma \Rightarrow Q \approx 1/\gamma$.

(ii) If $\gamma \simeq T_2$, then $Q \approx 1/T_2$, identical to the photon lifetime/escape factor q.

Answer: $Q = \frac{g_0}{\gamma(g_0 - \gamma)}$, so $Q \to 1/\gamma$ (high pump) and $Q \to 1/T_2 = q$ when γ is set by the output coupler.

C) Qualitative / Descriptive (5)

Q1. FM vs. intensity modulation (IM): why FM wins for sensitivity

Solution

- FM/phase-modulation with lock-in at Ω converts lineshapes to derivatives and shifts detection to a narrow band where technical $1/f$ noise is low.
- Common-mode drifts (slow intensity drift, window absorption) largely vanish in the derivative signal, while IM remains vulnerable.
- Phase modulation creates symmetric sidebands; without absorption, beat signals cancel → excellent baseline suppression.
- **Answer:** FM/PM + lock-in yields derivative signals with strong noise rejection and baseline stability, outperforming IM for small absorptions.

Q2. External enhancement cavity vs. multipass cell

Solution

- **Multipass cells**: simple, robust, guaranteed long L_{eff}, but limited finesse; residual etaloning must be managed.
- **External cavities**: large intracavity power $P_{\text{int}} = P_0/(1-R)$ and narrow spatial modes → higher peak intensity and better overlap but require **mode matching**, active length control with tunable lasers, and isolation to prevent feedback.
- **Answer:** Cavities deliver higher build-up but at higher alignment/control complexity; multipass cells are simpler but with lower enhancement.

Q3. Why "two-tone" FM with downconversion?

Solution

- At $\Omega \gtrsim$ hundreds of MHz–GHz, technical noise approaches the photon (shot) noise floor.
- Lock-in electronics cannot directly demodulate at GHz; two-tone FM amplitude-modulates the high-frequency phase drive so the detection occurs at a convenient kHz–MHz after **mixing** (downconversion) while preserving high-Ω noise benefits.
- **Answer:** It keeps the quantum-noise advantage of high-Ω modulation while enabling low-frequency lock-in detection.

Q4. Mode competition as a spectral analyzer (ICLAS)

Solution

- In multimode operation, an intracavity absorber increases loss for any mode overlapping its line, reducing that mode's intensity.
- Gain shared across modes (homogeneous broadening) lets the **other modes** steal gain → the absorbing mode can be strongly suppressed, creating **spectral holes** in the output.

- Dispersing the output (spectrograph/OMA) directly maps the absorber's spectrum.
- **Answer:** Mode competition turns absorption into deep "holes" at line positions, enabling very sensitive broadband recording.

Q5. Why time-resolved ICLAS (gate before the modes drift)?

Solution

- In real multimode lasers, mode frequencies wander; over times longer than the mean mode lifetime t_m, modal structure averages out, degrading quantitative absorption retrieval.
- Gating the measurement at $0 < t < t_m$ captures the instantaneous spectrum with very long effective path $L_{\text{eff}} = ct$ and strong holes, before mode diffusion blurs them.
- **Answer:** Early-time gating ($t < t_m$) preserves large effective paths and deep, well-registered absorption features.

(Optional) Instructor Notes

- Use **N3** to connect mechanical dither to GHz-scale frequency swings.
- Pair **A5** with **N5** to emphasize near-threshold vs. high-pump tradeoffs in ICLAS.
- **N4/Q1/Q3** make a coherent mini-module on FM/PM spectroscopy and noise.

Chapter 1.2.4 Problems

Problem Set — §1.2.4 Cavity Ring-Down Spectroscopy (CRDS)

Conventions used below (to keep units consistent with the textbook formulas):

- Use $c = 3.00 \times 10^{10}$ cm s^{-1} when α is in cm^{-1} and L in cm.
- Cavity length L denotes *mirror separation*.
- Mirror transmission+loss $T + A = 1 - R$ when additional losses are lumped into A.
- Empty-cavity decay time $\tau_2 = \frac{L/c}{T+A} \approx \frac{L/c}{1-R}$.
- With absorber: $\tau_1 = \frac{L/c}{T+A+\alpha L}$.
- Key relation: $\frac{1}{\tau_1} - \frac{1}{\tau_2} = c\,\alpha$.

A) Numerical (5)

N1. Extracting α from measured decay times

A ring-down cavity has $L = 100$ cm and very low scattering loss so that $T + A = 1 - R = 2.0 \times 10^{-4}$. With a sample inside, you measure $\tau_1 = 45.5\ \mu$s; without the sample, $\tau_2 = 50.0\ \mu$s. Estimate α.

Solution

1. Use $1/\tau_1 - 1/\tau_2 = c\alpha$.
2. Convert to seconds: $\tau_1 = 45.5 \times 10^{-6}$ s, $\tau_2 = 50.0 \times 10^{-6}$ s.
3. Compute difference:

$$\frac{1}{\tau_1} - \frac{1}{\tau_2} = \frac{1}{45.5 \times 10^{-6}} - \frac{1}{50.0 \times 10^{-6}} \approx (2.1989 - 2.0000) \times 10^4\ \text{s}^{-1} = 1.989 \times 10^3\ \text{s}^{-1}.$$

4. Solve for α: $\alpha = \frac{1.989 \times 10^3}{3.00 \times 10^{10}} = 6.63 \times 10^{-8}$ cm^{-1}.

Answer: $\boxed{\alpha \approx 6.6 \times 10^{-8}\ \text{cm}^{-1}}$.

N2. How mirror reflectivity controls τ (and sensitivity)

For a cavity with $L = 50$ cm:

(a) Compute τ_2 for $R = 0.9990$ and for $R = 0.9999$.

(b) What is the ratio of the two empty-cavity decay times?

Solution

Use $\tau_2 = \frac{L/c}{1-R} = \frac{50/3.00\times10^{10}}{1-R}$ s.

(a)

- $R = 0.9990 \Rightarrow 1 - R = 1.0 \times 10^{-3}$:
- $\tau_2 = \frac{1.667\times10^{-9}}{1.0\times10^{-3}} = 1.667 \times 10^{-6}$ s $= 1.67\ \mu$s.
- $R = 0.9999 \Rightarrow 1 - R = 1.0 \times 10^{-4}$:
- $\tau_2 = \frac{1.667\times10^{-9}}{1.0\times10^{-4}} = 1.667 \times 10^{-5}$ s $= 16.7\ \mu$s.
- (b) Ratio $= 16.7/1.67 = 10$.

Answer: $\boxed{\tau_2(0.9990) = 1.67\ \mu\text{s},\ \tau_2(0.9999) = 16.7\ \mu\text{s};\ \text{ratio} = 10}$.

N3. Minimum detectable α from a timing resolution

A setup (same as N2 with $R = 0.9999$, $L = 50$ cm) has a single-shot timing uncertainty $\delta(\Delta\tau) = 20$ ns for measuring $\Delta\tau = \tau_2 - \tau_1$. Estimate the **single-shot** $\alpha_{\min}$ using

$$\alpha \approx \frac{\Delta(1/\tau)}{c} \approx \frac{\Delta\tau}{c\,\tau^2},$$

with $\tau \approx \tau_2 = 16.7\ \mu$s.

Solution

1. $\tau = 16.7 \times 10^{-6}$ s $\Rightarrow \tau^2 = 2.79 \times 10^{-10}$ s^2.
2. $\alpha_{\min} \approx \frac{20\times10^{-9}}{(3.00\times10^{10})\,(2.79\times10^{-10})}$
3. $= \frac{2.0\times10^{-8}}{8.37} \approx 2.39 \times 10^{-9}$ cm^{-1}.

Answer: $\boxed{\alpha_{\min} \sim 2.4 \times 10^{-9} \text{ cm}^{-1} \text{ (single shot)}}$.

(Averaging N shots ideally improves by $1/\sqrt{N}$.)

N4. Effective path length and improvement factor

For $L = 100$ cm and $R = 0.9998$:

(a) Compute $L_{\text{eff}} = \frac{L}{1-R}$.

(b) What is the enhancement factor $\frac{L_{\text{eff}}}{L}$ relative to a single pass?

Solution

(a) $1 - R = 2.0 \times 10^{-4} \Rightarrow L_{\text{eff}} = 100 \text{ cm}/(2.0 \times 10^{-4}) = 5.0 \times 10^5 \text{ cm} = 5.0 \text{ km}$.

(b) Enhancement $= 1/(1 - R) = 5000$.

Answer: $\boxed{L_{\text{eff}} = 5.0 \text{ km},\ \text{enhancement} = 5.0 \times 10^3}$.

N5. Round-trip time, pulse regime, and heterodyne decay

A cavity has $L = 75$ cm, $R = 0.9998$.

(a) Find the round-trip time $T_R = 2L/c$.

(b) Empty-cavity decay time τ_2?

(c) In heterodyne-detected CRDS, what is the decay time constant of the beat term?

Solution

(a) $T_R = 2 \times 75/3.00 \times 10^{10} = 5.00 \times 10^{-9}$ s $= 5$ ns.

(b) $\tau_2 = \frac{L/c}{1-R} = \frac{75/3.00\times10^{10}}{2.0\times10^{-4}} = 1.25 \times 10^{-6}$ s $= 1.25\ \mu$s.

(c) Intensity decays $\propto e^{-t/\tau}$; field amplitude $\propto e^{-t/(2\tau)}$. The heterodyne term $\propto E_S E_{LO}$ decays with time constant 2τ.

Answer: $\boxed{T_R = 5 \text{ ns},\ \tau_2 = 1.25\ \mu\text{s},\ \text{heterodyne decay time} = 2\tau_2 = 2.50\ \mu\text{s}}$.

B) Analytical / Symbolic (5)

A1. Derive the exponential ring-down and τ

Start with a pulse entering a cavity of length L with net per-pass loss $T + A + \alpha L$. Show that the time-averaged transmitted power decays exponentially with

$$P(t) = P_1\, e^{-t/\tau}, \quad \boxed{\tau = \frac{L/c}{T + A + \alpha L}}.$$

Solution

- After n round trips: $P_n = P_1\,[R^2 e^{-2\alpha L}]^n = P_1\, e^{-2n[(1-R)+\alpha L]} \approx P_1 e^{-2n[(T+A)+\alpha L]}$.
- Pulses are spaced by $T_R = 2L/c \Rightarrow t = 2nL/c$. Substitute $n = t/(2L/c)$:

$$P(t) = P_1 \exp\left[-\frac{t}{L/c}\,(T + A + \alpha L)\right] = P_1 e^{-t/\tau}.$$

Thus $\tau = (L/c)/(T + A + \alpha L)$.

Answer: As boxed.

A2. Show $1/\tau_1 - 1/\tau_2 = c\alpha$

With absorber $\tau_1 = \frac{L/c}{T+A+\alpha L}$; empty $\tau_2 = \frac{L/c}{T+A}$. Prove the difference formula.

Solution

$$\frac{1}{\tau_1} - \frac{1}{\tau_2} = \frac{c}{L}[(T + A + \alpha L) - (T + A)] = \frac{c}{L}(\alpha L) = c\alpha.$$

Answer: $\boxed{1/\tau_1 - 1/\tau_2 = c\alpha}$.

A3. Effective path length L_{eff}

Show that the effective absorption path equals $L_{\text{eff}} = L/(1-R)$.

Solution

A fraction $(1-R)$ of the intracavity power is lost per *half* round trip (one pass). The average number of passes equals $1/(1-R)$. Each pass traverses length L. Hence

$$L_{\text{eff}} = \frac{1}{1-R}\, L.$$

Answer: $\boxed{L_{\text{eff}} = L/(1-R)}$.

A4. Propagate timing uncertainty to $\delta\alpha$

Given $\alpha = \frac{1}{c}\left(\frac{1}{\tau_1} - \frac{1}{\tau_2}\right)$ and independent uncertainties $\delta\tau_1 = \delta\tau_2 = \delta\tau$, derive an approximate $\delta\alpha$ for $\tau_1 \approx \tau_2 \approx \tau$.

Solution

- Sensitivities: $\frac{\partial\alpha}{\partial\tau_1} = -\frac{1}{c\,\tau_1^2}$, $\frac{\partial\alpha}{\partial\tau_2} = +\frac{1}{c\,\tau_2^2}$.
- Variance: $\delta\alpha^2 = \left(\frac{1}{c}\right)^2\left(\frac{\delta\tau^2}{\tau_1^4} + \frac{\delta\tau^2}{\tau_2^4}\right) \approx \left(\frac{1}{c}\right)^2 \frac{2\,\delta\tau^2}{\tau^4}$.
- Hence $\boxed{\delta\alpha \approx \frac{\sqrt{2}\,\delta\tau}{c\,\tau^2}}$.
- Equivalently, measuring $\Delta\tau$ directly with uncertainty $\delta(\Delta\tau) \approx \sqrt{2}\,\delta\tau$ and using $\alpha \approx \frac{\Delta\tau}{c\,\tau^2}$ yields the same result.

Answer: $\boxed{\delta\alpha \approx \frac{\sqrt{2}\,\delta\tau}{c\,\tau^2}}$ (for $\tau_1 \simeq \tau_2$).

A5. Heterodyne CRDS beat-term decay

Let the transmitted **intensity** decay as $I_S(t) = I_{S0}\, e^{-t/\tau}$. Show that the interference term with a strong, constant local oscillator E_{LO} decays as $\propto e^{-t/(2\tau)}$, i.e. with time constant 2τ.

Solution

- Field amplitude $|E_S(t)| \propto \sqrt{I_S(t)} = \sqrt{I_{S0}}\, e^{-t/(2\tau)}$.
- Interference term $\propto 2E_{LO}E_S(t)\cos(2\pi\delta\nu t + \phi)$ thus decays $\propto e^{-t/(2\tau)}$.
- Therefore the measured beat-envelope time constant is 2τ.
- **Answer:** $\boxed{\text{Beat envelope } \propto e^{-t/(2\tau)} \Rightarrow \text{time constant} = 2\tau}$.

C) Qualitative / Descriptive (5)

Q1. CRDS vs. intracavity absorption (ICLAS): what's fundamentally different?

Solution (steps)

1. **Shared idea:** Enormous effective path length via multiple traversals.
2. **CRDS:** Measures *time constant* of cavity energy decay (intensity ring-down) → absolute α from time, largely independent of shot-to-shot laser intensity.
3. **ICLAS:** Exploits gain and mode competition inside (active or external) cavities; sensitivity manifests as mode quenching/spectral holes; requires careful modeling of gain/loss dynamics.
4. **Answer:** CRDS is a *time-domain loss metrology*; ICLAS is a *gain-competition spectroscopy*—both enhance path, but the measured observables and noise sensitivities differ.

Q2. Why mode matching and TEM_{00} matter at very high R

Solution (steps)

1. As $R \to 1$, diffraction/scatter losses can dominate A.
2. Higher-order transverse modes suffer larger diffraction losses and short τ.
3. Mode matching to TEM_{00} minimizes A, maximizes τ, and yields single-exponential decays (clean fits).
4. **Answer:** Proper mode matching suppresses parasitic losses and ensures long, single-mode ring-down needed for ultimate sensitivity.

Q3. Practical conditions for high sensitivity (textbook criteria)

Solution (steps)

1. Excited cavity-mode bandwidth $\delta\omega_R = 1/T_R$ should be **smaller** than absorption width $\delta\omega_a$.
2. Laser bandwidth $\delta\omega_L \lesssim \delta\omega_a$ to avoid overfilling many modes.
3. Relaxation T_R longer than excited-state lifetime $T_{\rm exc}$ so that the cavity probes absorption rather than transient emission dynamics.
4. **Answer:** Choose cavity length, mirror curvature, and laser pulsewidth so that $\delta\omega_R < \delta\omega_a$ and $\delta\omega_L \lesssim \delta\omega_a$ while keeping $T_R>T_{\rm exc}$.

Q4. Advantages/limits of CRDS in practice

Solution (steps)

Pros:

- Decay time is intensity-independent → robust to laser power fluctuations.
- High repetition rates allow strong averaging → high SNR.
- With $R \gtrsim 0.9999$, $L_{\mathrm{eff}} \sim 10^4 L$ is routine.
- **Cons:**

- Cavity mode structure can gate what you see; synchronous length tuning may be needed with narrowband lasers.
- Requires *very* high-R mirrors (costly; wavelength-specific); alignment and isolation critical.
- **Answer:** CRDS is extremely sensitive and power-robust, but demands superb optics/alignment and sometimes active cavity control.

Q5. CALOS and phase-shift ring-down: when and why?

Solution (steps)

1. **CALOS:** cw laser scans; when on resonance, power builds; then input is shut off and decay is recorded—benefits from cw laser's low technical noise and efficient averaging → very low α limits.
2. **Phase-shift method:** With amplitude-modulated cw input, the cavity imparts phase $\tan\varphi = \Omega\tau$; measuring $\varphi(\Omega)$ yields τ without nanosecond timing.
3. **Answer:** CALOS excels for ultra-high sensitivity with cw sources; phase-shift CRDS trades timing complexity for phase metrology using lock-in techniques.

(Optional) Instructor Hints

- **N1/N3** pair nicely to show how $\Delta\tau$ resolution translates to α limits and why higher R is priceless.
- Use **A5** with **N5** to motivate heterodyne CRDS's SNR advantage (beat term decays with 2τ).
- **Q3/Q4** can anchor a lab design discussion (mirror choices, curvature, spot size, mode matching).

Chapter 1.3

Problems

Problem Set — §1.3 Direct Determination of Absorbed Photons

Conventions (consistent with the section):

- $n_a = N_i\,\sigma_{ik}\,n_L\,\Delta x$ absorbed photons/s.
- Fluorescence photons/s: $n_{\mathrm{Fl}} = n_a\,\eta_k$.
- Detected photoelectrons/s: $n_{pe} = n_a\,\eta_k\,\eta_{ph}\,\delta$.
- Photon flux from laser power P at wavelength λ: $n_L = P\,\lambda/(hc)$.
- $h = 6.626 \times 10^{-34}$ J s, $c = 3.00 \times 10^{8}$ m s^{-1}.
- Collection factor $\delta = d\Omega/4\pi$. For a circular cone half-angle θ: $\delta = (1 - \cos\theta)/2$.

A) Numerical (5)

N1. Turning absorbed photons into counts

A probe volume of length $\Delta x = 0.20$ cm contains $N_i = 2.0 \times 10^{7}$ cm^{-3}. The transition cross section is $\sigma_{ik} = 3.0 \times 10^{-17}$ cm^2. A laser delivers $n_L = 5.0 \times 10^{16}$ s^{-1} photons (≈ 8 mW at 500 nm). Fluorescence quantum efficiency $\eta_k = 0.90$; PMT quantum efficiency $\eta_{ph} = 0.25$; collection $\delta = 0.12$.

Compute the detected photoelectron rate n_{pe}.

Solution

1. Absorption probability per photon: $N_i\sigma_{ik}\Delta x = (2.0 \times 10^{7})(3.0 \times 10^{-17})(0.20) = 1.2 \times 10^{-10}$.
2. Absorptions/s: $n_a = n_L \times 1.2 \times 10^{-10} = 5.0 \times 10^{16} \times 1.2 \times 10^{-10} = 6.0 \times 10^{6}$ s^{-1}.
3. Detected counts: $n_{pe} = n_a\,\eta_k\,\eta_{ph}\,\delta = 6.0 \times 10^{6} \times 0.90 \times 0.25 \times 0.12$.
4. Efficiency product $= 0.027 \rightarrow n_{pe} = 1.62 \times 10^{5}$ s^{-1}.

Answer: $\boxed{n_{pe} \approx 1.6 \times 10^5 \text{ counts/s}}$.

N2. Shot-noise detectability with dark counts

Your cooled PMT has a dark rate of $20\ \text{s}^{-1}$. Over a 1 s gate, what **minimum** signal count rate n_{pe} achieves $\text{SNR} = 5$ (Poisson: $\text{SNR} = N_s/\sqrt{N_s + N_d}$)?

Solution

Let $N_s = n_{pe} \times 1\ \text{s}$, $N_d = 20$. Solve $N_s^2 = 25(N_s + 20) \Rightarrow N_s^2 - 25N_s - 500 = 0$.

Discriminant $= 625 + 2000 = 2625 \Rightarrow \sqrt{2625} \approx 51.24$.

$N_s = \frac{25+51.24}{2} \approx 38.1$ (positive root).

$n_{pe} \approx 38\ \text{s}^{-1}$.

Answer: $\boxed{n_{pe} \approx 38 \text{ counts/s}}$ for $\text{SNR} = 5$ in 1 s.

N3. Collection factor from cone half-angle

Your optics accept a half-angle $\theta = 30°$. For isotropic fluorescence, compute δ, then the count rate if $n_a = 2.0 \times 10^6\ \text{s}^{-1}$, $\eta_k = 1$, $\eta_{ph} = 0.20$.

Solution

1. $\delta = (1 - \cos\theta)/2 = (1 - 0.8660)/2 = 0.0670$.
2. $n_{pe} = n_a\, \eta_k\, \eta_{ph}\, \delta = 2.0 \times 10^6 \times 1 \times 0.20 \times 0.0670 \approx 2.68 \times 10^4\ \text{s}^{-1}$.

Answer: $\boxed{\delta \approx 0.067, \quad n_{pe} \approx 2.7 \times 10^4 \text{ counts/s}}$.

N4. Why the IR is hard: a quantitative comparison

Compare detected rates for **the same** n_a in visible and IR when

VIS: $\eta_k = 1.0,\ \eta_{ph} = 0.20,\ \delta = 0.10$;

IR: $\eta_k = 0.30,\ \eta_{ph} = 0.020,\ \delta = 0.030.$

Find n_{pe}^{IR}/n_{pe}^{VIS}.

Solution

Ratio $= \frac{\eta_k^{IR}\eta_{ph}^{IR}\delta^{IR}}{\eta_k^{VIS}\eta_{ph}^{VIS}\delta^{VIS}} = \frac{0.30\times0.020\times0.030}{1.0\times0.20\times0.10} = \frac{1.8\times10^{-4}}{2.0\times10^{-2}} = 9.0\times10^{-3}.$

Answer: $\boxed{n_{pe}^{IR} \approx 0.9\% \times n_{pe}^{VIS}}$ (≈ two orders of magnitude less).

N5. Single-atom "photon burst" detectability

A true two-level atom traverses the laser spot in $T = 20\ \mu s$. The excited-state lifetime is $\tau = 10$ ns. Assume the burst limit $n_{\max} = T/(2\tau)$ applies. With $\eta_k = 1,\ \delta = 0.08,\ \eta_{ph} = 0.20,$ estimate detected counts **per atom** and SNR if background contributes 0.10 counts in the 20 µs gate.

Solution

1. $n_{\max} = T/(2\tau) = \frac{2.0\times10^{-5}}{2.0\times10^{-8}} = 10^3$ photons/atom.
2. Detected per atom: $N_{pe} = n_{\max}\,\delta\,\eta_{ph} = 1000\times0.08\times0.20 = 16$ counts.
3. SNR $= \frac{16}{\sqrt{16+0.10}} \approx \frac{16}{4.01} \approx 4.0.$

Answer: $\boxed{N_{pe} \approx 16 \text{ counts/atom},\ \text{SNR} \approx 4}$ → single-atom detection is feasible.

B) Analytical / Symbolic (5)

A1. From absorption to detected counts (derive Eq. 1.36)

Show: $n_{pe} = N_i\,\sigma_{ik}\,n_L\,\Delta x\ \eta_k\,\eta_{ph}\,\delta.$

Solution

1. Absorptions/s: $n_a = N_i\sigma_{ik}n_L\Delta x.$

2. Radiative yield: $n_{Fl} = n_a \, \eta_k$.
3. Geometric collection: $n_{Fl} \to n_{Fl} \, \delta$.
4. Photocathode conversion: $n_{pe} = n_{Fl} \, \delta \, \eta_{ph}$.
5. Combine to get the stated expression.

Answer: Derived as above.

A2. When does the excitation spectrum equal the absorption spectrum?

Show the condition: line intensities match only if η_k, η_{ph}, and δ are level- (and wavelength-) independent across the scan.

Solution

Measured signal $\propto N_i \sigma_{ik} \times \eta_k \eta_{ph}(\lambda) \delta$.

If $\eta_k \equiv 1$ (collision-free), η_{ph} flat, and δ constant (no anisotropy/diffusion loss), then $I_{Fl}(\lambda_L) \propto N_i \sigma_{ik}$. Otherwise, relative line intensities are distorted by the multiplicative factor.

Answer: $\boxed{\eta_k = \text{const},\ \eta_{ph} = \text{const},\ \delta = \text{const} \ \Rightarrow \ I_{excitation} \propto I_{absorption}}$.

A3. Geometry–collection relation

For a circular aperture radius a at distance R (viewing a point source), derive δ in terms of $\theta = \arctan(a/R)$ and give the small-angle limit.

Solution

Solid angle of a cone: $d\Omega = 2\pi(1 - \cos\theta)$.

$\delta = d\Omega/4\pi = (1 - \cos\theta)/2$.

Small θ: $\cos\theta \simeq 1 - \theta^2/2 \Rightarrow \delta \simeq \theta^2/4 \simeq a^2/(4R^2)$.

Answer: $\boxed{\delta = (1 - \cos\theta)/2 \ \simeq \ a^2/(4R^2) \text{ for } a \ll R}$.

A4. Shot-noise-limited $N_i^{\min}$ with background

Let the integration time be t and background n_b (counts/s). With $y \equiv n_{pe}t$ and target SNR, show

$$y = \frac{\mathrm{SNR}^2}{2}\left[1 + \sqrt{1 + \frac{4n_b t}{\mathrm{SNR}^2}}\right], \quad N_i^{\min} = \frac{y}{\sigma_{ik}\,\Delta x\, n_L\, \eta_k\, \eta_{ph}\, \delta\, t}.$$

Solution

$\mathrm{SNR}^2 = y^2/(y + n_b t) \Rightarrow y^2 - \mathrm{SNR}^2 y - \mathrm{SNR}^2 n_b t = 0.$

Solve quadratic for $y > 0$, then divide by the fluorescence gain factor from A1 to solve for N_i.

Answer: As boxed.

A5. Intracavity enhancement of LIF

Assume the excitation region sits in an external enhancement cavity with power build-up B (no saturation). Show $n_{pe}^{(\mathrm{cav})} = B\, n_{pe}^{(\mathrm{single})}$.

Solution

The local photon flux scales with intracavity power, $n_L \to B\, n_L$. A1 then gives $n_{pe} \propto n_L$; hence n_{pe} scales linearly with B.

Answer: $\boxed{n_{pe} \propto B \Rightarrow n_{pe}^{(\mathrm{cav})} = B\, n_{pe}^{(\mathrm{single})}}$.

C) Qualitative / Descriptive (5)

Q1. Designing for large δ: which optics and why?

Solution (steps)

1. **Parabolic mirror** around the interaction region → near-2π solid angle.

2. **Elliptical mirror + hemispherical back-reflector** → redirect "lost" half-space light into the acceptance cone; couple to a fiber (end-face at second focus) matched to spectrograph slit.
3. Keep refractive surfaces minimal → suppress scattered laser light into the detector.

Answer: Use reflective, near-hemispherical or elliptical collectors; minimize stray light to maximize usable δ.

Q2. Why excitation spectra can misreport relative intensities

Solution (steps)

- η_k varies with state (collisional quenching, internal conversion).
- $\eta_{ph}(\lambda)$ varies across broad fluorescence bands.
- δ varies if fluorescence is anisotropic or lifetimes are long (diffusion out of view).

Answer: Level- and wavelength-dependent η_k, η_{ph}, and δ skew line strengths even though positions are correct.

Q3. Why sensitivity drops in the IR

Solution (steps)

- IR detectors have low η_{ph} and higher noise than visible PMTs.
- Vibrational transitions have long radiative lifetimes → molecules leave the view before emitting → effective $\delta \downarrow$.
- At higher pressures, collisional deactivation competes → $\eta_k \downarrow$.

Answer: Simultaneous drops in η_{ph}, δ, and η_k make LIF far less sensitive in the IR.

Q4. Beating the background to reach ultra-low densities

Solution (steps)

- **Baffles/blackening** along the laser path; Brewster-angle windows to suppress reflections.
- **Spatial/temporal filtering:** orthogonal collection to laser beam; gated detection synced to excitation.
- **Spectral filtering:** notch or interference filters to block laser wavelength; detect red-shifted fluorescence.
- **Photon counting + averaging** to approach Poisson limits.

Answer: Aggressive stray-light management + synchronous photon counting unlocks densities down to $\sim 10^2\ \mathrm{cm}^{-3}$ (limited by residual scatter).

Q5. Filtered excitation spectra: when to use?

Solution (steps)

- Complex polyatomic spectra with overlapping absorptions or broad laser linewidth.
- Select a **single emission line** from one upper level via a spectrometer → detect only its fluorescence while scanning excitation.
- Sacrifices signal, but simplifies assignment and reveals level-specific structure.

Answer: Use filtered excitation when congestion obscures assignments; line-selective detection trades photons for clarity.

Chapter 1.3.2 Problems

Problem Set — §1.3.2 Photoacoustic Spectroscopy

Core relations (from the text):

- Absorbed energy per cycle (no saturation):

  $\Delta W = N_i\,\sigma_{ik}\,\Delta x\,(1-\eta_k)\,P_L\,\Delta t$

- Equipartition heating and pressure rise:

  $\Delta W = 1/2\,f\,V\,N\,k\,\Delta T, \qquad \Delta p = N\,k\,\Delta T = \frac{2\,\Delta W}{f\,V}$

- Microphone output:

  $S = \Delta p\,S_m = \frac{2\,N_i\,\sigma_{ik}}{f\,V}\,\Delta x\,(1-\eta_k)\,P_L\,\Delta t\,S_m$

- Chopping condition for full conversion to heat: $\Omega < 1/T$ (with relaxation time T).
- Resonant cell: optional acoustic gain factor G_{ac} multiplies Δp (and S).

A) Numerical (5)

N1. Baseline photoacoustic signal

A cell has $V = 40\ \mathrm{cm}^3$, $f = 6$, $\Delta x = 8\ \mathrm{cm}$, $S_m = 10\ \mathrm{mV/Pa}$. The gas contains $N_i = 1.5 \times 10^{11}\ \mathrm{cm}^{-3}$ absorbers with $\sigma_{ik} = 1.2 \times 10^{-16}\ \mathrm{cm}^2$. A laser of $P_L = 80\ \mathrm{mW}$ is chopped with duty window $\Delta t = 5.0 \times 10^{-4}\ \mathrm{s}$. Collisional quenching is complete ($\eta_k = 0$).

Compute Δp and the microphone output S.

Solution

$$\Delta W = N_i \sigma_{ik} \Delta x (1-\eta_k) P_L \Delta t$$

Convert $P_L \Delta t = 0.080 \times 5.0 \times 10^{-4} = 4.0 \times 10^{-5}\ \mathrm{J}$.

The dimensionless absorption factor:

$$N_i \sigma_{ik} \Delta x = (1.5 \times 10^{11})(1.2 \times 10^{-16})(8) = 1.44 \times 10^{-4}.$$

So $\Delta W = 1.44 \times 10^{-4} \times 4.0 \times 10^{-5} = 5.76 \times 10^{-9}\ \mathrm{J}$.

Pressure rise:

$$\Delta p = \frac{2\Delta W}{fV} = \frac{2(5.76 \times 10^{-9})}{6 \times 40 \times 10^{-6}} = 4.8 \times 10^{-5}\ \text{Pa}.$$

Signal:

$$S = \Delta p\, S_m = 4.8 \times 10^{-5} \times 10^{-2} = 4.8 \times 10^{-7}\ \text{V} = 0.48\ \mu\text{V}.$$

Answer: $\Delta p \approx 4.8 \times 10^{-5}$ Pa, $S \approx 0.48\ \mu$V.

N2. Minimum detectable concentration from electronics noise

Electronics noise is 3.0×10^{-8} V (1-s integration). Using the same parameters as N1, what is the minimum N_i for SNR $= 3$? (Assume linear regime; $\eta_k = 0$.)

Solution

Required signal $S_{\text{req}} = 3 \times 3.0 \times 10^{-8} = 9.0 \times 10^{-8}$ V.

Because $S \propto N_i$, scale from N1:

$$N_i^{\min} = N_i^{(N1)} \times \frac{S_{\text{req}}}{S^{(N1)}} = 1.5 \times 10^{11} \times \frac{9.0 \times 10^{-8}}{4.8 \times 10^{-7}} \approx 2.8 \times 10^{10}\ \text{cm}^{-3}.$$

Answer: $\boxed{N_i^{\min} \approx 2.8 \times 10^{10}\ \text{cm}^{-3}}$.

N3. Role of fluorescence yield η_k

Keep N1 parameters but now $\eta_k = 0.6$ (significant fluorescence escapes). What are the new Δp and S? What is the signal ratio $S(\eta_k = 0.6)/S(\eta_k = 0)$?

Solution

Scale by $(1 - \eta_k)$: factor $= 0.4$.

Thus $\Delta p = 0.4 \times 4.8 \times 10^{-5} = 1.92 \times 10^{-5}$ Pa.

$S = 0.4 \times 0.48\ \mu\text{V} = 0.192\ \mu\text{V}$.

Ratio $= 0.4$.

Answer: $\Delta p \approx 1.92 \times 10^{-5}$ Pa, $S \approx 0.19\ \mu$V; ratio 0.40.

N4. Acoustic resonance boost

With the same conditions as N1, the cell is driven at a strong longitudinal resonance giving an acoustic gain $G_{\mathrm{ac}} = 600$. Compute the boosted S. If wall-heating background contributes a baseline $S_{\mathrm{bg}} = 0.10\ \mu$V (non-resonant), what's the net SNR against that baseline only?

Solution

Boosted signal $S' = G_{\mathrm{ac}} S = 600 \times 0.48\ \mu\mathrm{V} = 288\ \mu\mathrm{V}$.

SNR vs baseline $= S'/S_{\mathrm{bg}} = 288/0.10 = 2880$.

Answer: $S' \approx 288\ \mu$V; SNR $\approx 2.9 \times 10^{3}$ vs that background.

N5. Multipass + intracavity enhancement

An acoustic cell sits inside a multipass optics giving $\Delta x_{\mathrm{eff}} = 40\ \mathrm{m}$ and within an external enhancement cavity with intensity build-up $q = 30$. Baseline single-pass values: $\Delta x_0 = 10\ \mathrm{cm}$, $P_{L,0} = 100\ \mathrm{mW}$ yielding $S_0 = 12\ \mu\mathrm{V}$.

Estimate the new S.

Solution

$S \propto \Delta x\, P_L$.

Δx factor $= 40\ \mathrm{m}/0.10\ \mathrm{m} = 400$.

P_L factor $= q = 30$.

Total factor $= 400 \times 30 = 1.2 \times 10^{4}$.

$S = S_0 \times 1.2 \times 10^{4} = 12\ \mu\mathrm{V} \times 1.2 \times 10^{4} = 144\ \mathrm{mV}$.

Answer: $\boxed{S \approx 0.144\ \mathrm{V}}$ (neglecting saturation/extra losses).

B) Analytical / Symbolic (5)

A1. Derive the pressure-signal formula

Show that, under $\Omega < 1/T$, the microphone output

$$S = \frac{2\,N_i\,\sigma_{ik}}{f\,V}\,\Delta x\,(1-\eta_k)\,P_L\,\Delta t\,S_m.$$

Solution

(i) Absorbed energy/cycle: $\Delta W = N_i \sigma_{ik} \Delta x (1-\eta_k) P_L \Delta t$.

(ii) Equipartition heating: $\Delta W = (1/2) f V N k \Delta T \Rightarrow \Delta T = 2\Delta W/(fVNk)$.

(iii) Ideal gas: $\Delta p = Nk\Delta T = 2\Delta W/(fV)$.

(iv) Microphone: $S = \Delta p S_m$. Combine to obtain the stated expression.

Answer: Derived as above.

A2. Pressure-signal scaling with volume and degrees of freedom

Given A1, prove the parametric scalings $S \propto 1/V$ and $S \propto 1/f$. Interpret physically.

Solution

From A1, S is inversely proportional to fV. Smaller V means the same heat raises temperature/pressure more; larger f (more accessible degrees of freedom) distributes the energy over more modes, lowering ΔT and Δp.

Answer: $\boxed{S \sim V^{-1}}$ (compact cells amplify) and $\boxed{S \sim f^{-1}}$ (fewer DOF → higher signal).

A3. Effect of incomplete quenching and internal reabsorption

If a fraction r of fluorescence is **reabsorbed** within the cell and thermalized, show that the effective factor is

$$(1-\eta_k) + r\,\eta_k = 1 - \eta_k(1-r).$$

Solution

Absorbed laser energy → heat fraction $= 1 - \eta_k$. Of the radiative fraction η_k, reabsorbed part $r\eta_k$ contributes to heating. Total heating fraction:

$$1 - \eta_k + r\eta_k = 1 - \eta_k(1 - r).$$

Insert this in A1 by replacing $(1 - \eta_k)$ with $1 - \eta_k(1 - r)$.

Answer: As shown; reabsorption mitigates the penalty of high η_k.

A4. Frequency choice: relaxation vs resonance

Let the thermo-mechanical response be approximated by a first-order low-pass $H_{\mathrm{th}}(\Omega) = 1/\sqrt{1 + (\Omega T)^2}$ and an acoustic resonance factor $H_{\mathrm{ac}}(\Omega) = 1/\sqrt{(1 - \Omega^2/\Omega_0^2)^2 + (\Omega/\Omega_0 Q)^2}$.

Explain why optimal drive is $\Omega \approx \Omega_0$ **with** $\Omega_0 T \ll 1$.

Solution

Maximize $|H| = |H_{\mathrm{th}} H_{\mathrm{ac}}|$:

- If $\Omega = \Omega_0$, $|H_{\mathrm{ac}}| = Q$ (peak).
- To avoid thermal roll-off, need $|H_{\mathrm{th}}| \approx 1 \Rightarrow \Omega T \ll 1$.
- Thus choose resonance well below the relaxation cutoff: $\boxed{\Omega_0 T \ll 1}$.

Answer: Drive at the cell's acoustic resonance but keep it below the thermal relaxation corner.

A5. Differential suppression of wall-heating background

Suppose non-resonant wall heating produces a pressure term Δp_{wall} with flat frequency response, while the true signal has G_{ac} at resonance. Show that measuring on-resonance minus off-resonance yields a net improvement factor $\approx G_{\mathrm{ac}}$ in signal over background.

Solution

On resonance: $p_{\mathrm{on}} = G_{\mathrm{ac}}\, \Delta p_{\mathrm{true}} + \Delta p_{\mathrm{wall}}$.

Off resonance: $p_{\mathrm{off}} \approx \Delta p_{\mathrm{true}} + \Delta p_{\mathrm{wall}}$.

Differencing: $p_{\mathrm{on}} - p_{\mathrm{off}} \approx (G_{\mathrm{ac}} - 1)\Delta p_{\mathrm{true}}$ with walls canceled. For $G_{\mathrm{ac}} \gg 1$, enhancement $\sim G_{\mathrm{ac}}$.

Answer: Differential (on−off) turns the acoustic gain into background suppression by $\sim G_{\mathrm{ac}}$.

C) Qualitative / Descriptive (5)

Q1. PAS vs. LIF: when does PAS win?

Solution

- **PAS** benefits when $\eta_k \to 0$ (IR vibrational excitations at ≥ mbar), strong collisional quenching, and in complex gas mixtures at pressure (no need for spectral isolation of fluorescence).
- **LIF** excels at low pressure with high η_k (electronic transitions, VIS/UV) and excellent detectors.
- **Answer:** Use PAS for IR, higher pressures, trace-gas monitoring; use LIF for VIS/UV, low pressure, state-resolved work.

Q2. Practical tricks to tame stray-light background

Solution

- Brewster or AR-coated windows; blackened, baffled apertures.
- Orthogonal collection geometry; minimize window hotspots.
- Drive at an **acoustic resonance** and lock-in at that frequency; differential on/off-resonance subtraction.
- **Answer:** Optical hygiene + resonant, phase-sensitive detection suppress wall-heating artifacts.

Q3. Why small cells help (but what's the catch?)

Solution

- $S \propto 1/V$: smaller V boosts pressure per absorbed joule.
- Trade-offs: Δx might shrink; boundary heat losses grow if Ω is too low (need $\Omega T \ll 1$); microphone placement and mode patterns become critical.
- **Answer:** Shrink V to raise S, but preserve path length and operate above thermal-loss corner.

Q4. Energy-transfer PAS (Patel scheme): what's the idea?

Solution

Pump species A to $v = 1$; resonant collisions populate B($v = 1$); probe B by weak tunable laser on $v = 1 \rightarrow 2$; detect with PAS. Lets you study B even if no strong pump line exists for B.

Answer: Use collisional vibrational transfer to "borrow" pumpability from A and spectroscopically access B.

Q5. PAS signature at dissociation thresholds

Solution

Below threshold, absorbed energy → heat → strong PAS signal. Above threshold, energy goes into bond breaking (potential energy), not thermalization → PAS drops abruptly.

Answer: A sharp PAS decrease flags the dissociation limit and can be used to measure D_0.

(Optional) Instructor notes

- Pair **N1–N3–A3** to emphasize $(1 - \eta_k)$ (and reabsorption) in PAS vs LIF.
- **N4–A5** make a clean lab on resonant detection and background subtraction.
- **N5** ties PAS to optical path-extension strategies from §1.2 (multipass/external cavity).

Chapter 1.3.3 Problems

Problem Set — §1.3.3 Optothermal Spectroscopy

Core relations from the section:

- Energy deposited per second by excited molecules reaching the bolometer:
- $\frac{dQ}{dt} = N\,\Delta E = N\,h\nu$.
- Thermal balance of a bolometer with heat capacity C and conductance G:
- $Nh\nu = C\,\frac{dT}{dt} + G\,(T - T_0)$.
- Steady state (with chopping slow enough):
- $\Delta T \equiv T - T_0 = \frac{Nh\nu}{G}$.
- Bolometer time constant: $\tau = \frac{C}{G}$. For lock-in detection with chopping frequency f_{chop}, choose $\tau \ll 1/f_{\text{chop}}$.
- Flight-time condition for molecular beams: if the radiative lifetime $\tau_{rad} \gg t = d/v$, excited molecules carry their added energy $\Delta E = h\nu$ to the detector; otherwise only a survival fraction contributes.

A) Numerical (5)

N1. Minimum molecular rate for the detection limit

A helium-cooled bolometer can detect down to $(dQ/dt)_{\min} = 1.0 \times 10^{-14}$ W. For an IR transition at $\lambda = 4.50$ μm, what minimum number of excited molecules per second $N_{\min}$ must hit the bolometer?

Solution

1. Photon energy $h\nu = hc/\lambda$.
2. $h = 6.626 \times 10^{-34}$ J·s, $c = 3.00 \times 10^{8}$ m/s, $\lambda = 4.50 \times 10^{-6}$ m.
3. $h\nu = \frac{6.626\times10^{-34}\cdot3.00\times10^{8}}{4.50\times10^{-6}} = 4.42 \times 10^{-20}$ J.

4. $N_{\min} = (dQ/dt)_{\min}/(h\nu) = \frac{1.0\times10^{-14}}{4.42\times10^{-20}} \approx 2.26 \times 10^{5}\ \text{s}^{-1}$.

Answer: $\boxed{N_{\min} \approx 2.3 \times 10^{5}\ \text{molecules/s}}$.

N2. Steady temperature rise with given conductance

A beam of excited molecules delivers $N = 3.0 \times 10^{6}\ \text{s}^{-1}$ at $\lambda = 3.00\ \mu\text{m}$. The bolometer's thermal conductance is $G = 2.0 \times 10^{-7}$ W/K. Find the steady ΔT.

Solution

1. $h\nu = hc/\lambda = \frac{6.626\times10^{-34}\cdot3.00\times10^{8}}{3.00\times10^{-6}} = 6.63 \times 10^{-20}$ J.
2. $dQ/dt = N h\nu = 3.0 \times 10^{6} \cdot 6.63 \times 10^{-20} = 1.99 \times 10^{-13}$ W.
3. $\Delta T = (dQ/dt)/G = \frac{1.99\times10^{-13}}{2.0\times10^{-7}} = 9.95 \times 10^{-7}$ K.

Answer: $\boxed{\Delta T \approx 1.0\ \mu\text{K}}$.

N3. Chopping frequency constraint from time constant

The bolometer has $C = 1.0 \times 10^{-9}$ J/K and $G = 2.0 \times 10^{-7}$ W/K.

(a) Compute τ. (b) What is a safe **maximum** chopping frequency f_{chop} so that $\tau \leq 0.1/f_{\text{chop}}$ (i.e., $\Omega\tau \lesssim 0.6$ for near-flat response)?

Solution

(a) $\tau = C/G = \frac{1.0\times10^{-9}}{2.0\times10^{-7}} = 5.0 \times 10^{-3}\ \text{s} = 5\ \text{ms}$.

(b) Require $\tau \leq 0.1/f \Rightarrow f \leq 0.1/\tau = 0.1/0.005 = 20$ Hz.

Answer: $\boxed{\tau = 5\ \text{ms}, \quad f_{\text{chop}} \lesssim 20\ \text{Hz (safe)}}$.

N4. Survival fraction during flight

The laser–detector distance is $d = 5.0$ cm. Molecular speed $v = 600$ m/s. Radiative lifetime $\tau_{rad} = 5.0$ ms. If $N_0 = 1.0 \times 10^6$ s^{-1} molecules are excited, how many contribute at the bolometer and what is the fraction?

Solution

1. Flight time $t = d/v = 0.05/600 = 8.33 \times 10^{-5}$ s $= 0.083$ ms.
2. Survival probability (no radiative decay before arrival): $P_s = e^{-t/\tau_{rad}} = e^{-0.083/5.0} = e^{-0.0166} \approx 0.9835.$
3. Contributing rate $N = N_0 P_s = 9.84 \times 10^5$ s^{-1}.

Answer: $\boxed{N \approx 9.8 \times 10^5 \text{ s}^{-1} \ (98.3\% \text{ survive})}$.

N5. How much cavity build-up is needed?

Your single-pass configuration gives $dQ/dt_0 = 2.0 \times 10^{-15}$ W at resonance—below the 1.0×10^{-14} W detection limit. An enhancement cavity increases the intracavity power by a factor B (no saturation; perfect overlap), hence $dQ/dt = B\, dQ/dt_0$. Find the minimum B.

Solution

$B_{\min} = (dQ/dt)_{\min}/(dQ/dt)_0 = (1.0 \times 10^{-14})/(2.0 \times 10^{-15}) = 5.$

Answer: $\boxed{B_{\min} = 5}$.

B) Analytical / Symbolic (5)

A1. Thermal response and steady state

Show that the bolometer equation $Nh\nu = C\frac{dT}{dt} + G(T - T_0)$ yields the steady rise $\Delta T = \frac{Nh\nu}{G}$ and time constant $\tau = \frac{C}{G}$.

Solution

Set $x(t) = T(t) - T_0$. Then $Nh\nu = C\dot{x} + Gx$. The homogeneous solution decays as $e^{-t/\tau}$ with $\tau = C/G$. The particular solution is constant $x_p = (Nh\nu)/G$. Thus $x(t) = x_p + [x(0) - x_p]e^{-t/\tau}$, so steady $\Delta T = x_p = Nh\nu/G$.

Answer: $\boxed{\Delta T = Nh\nu/G,\ \tau = C/G}$.

A2. Frequency response to sinusoidal chopping

If the excitation rate is sinusoidally modulated: $N(t) = \bar{N} + \tilde{N}\cos\Omega t$, show that the temperature modulation amplitude is

$$|\widetilde{\Delta T}| = \frac{\tilde{N}\, h\nu}{\sqrt{G^2 + (\Omega C)^2}} = \frac{\tilde{N}\, h\nu/G}{\sqrt{1 + (\Omega\tau)^2}}.$$

Solution

Linearize about $\bar{N}$: the AC equation is $C\,\dot{\delta T} + G\,\delta T = \tilde{N}h\nu\cos\Omega t$. Steady sinusoidal response has amplitude $|\delta T| = (\tilde{N}h\nu)/\sqrt{G^2 + (\Omega C)^2}$. Substitute $\tau = C/G$ to get the second form.

Answer: As stated.

A3. Survival probability and effective heat rate

Let the radiative decay be exponential with lifetime τ_{rad}. For flight time t, **show** that the effective deposited power is

$$\left(\frac{dQ}{dt}\right)_{\text{eff}} = N_0\, h\nu\, e^{-t/\tau_{rad}}.$$

Solution

Each excited molecule contributes $h\nu$ only if it survives to the bolometer. The survival probability is $e^{-t/\tau_{rad}}$. For an excitation rate N_0, the arrival rate is $N_0 e^{-t/\tau_{rad}}$. Multiply by $h\nu$.

Answer: $\boxed{(dQ/dt)_{\text{eff}} = N_0 h\nu\, e^{-t/\tau_{rad}}}$.

A4. Intercepted-flux scaling with detector area

Let the beam carry a uniform flux density Φ (excited molecules per second per area) across diameter D. If the bolometer's effective collection area is increased from A_1 (bare Si) to A_2 using a sapphire "puck", **show** that the excited arrival rate scales as $N = \Phi A$ and the signal gain is $g = A_2/A_1$ (assuming the sapphire adds negligible heat capacity at 1.5 K).

Solution

Molecules per second hitting the sensor = flux density × area: $N = \Phi A$. With the sapphire spreading the capture area to A_2, $N_2/N_1 = A_2/A_1$. If added heat capacity is negligible (Debye $C \propto T^3$ at 1.5 K), $\Delta T \propto N$, so the signal scales by $g = A_2/A_1$.

Answer: $\boxed{N \propto A,\ \text{gain}\ g = A_2/A_1}$.

A5. Multipass/enhancement factor

If an optical geometry passes the laser through the excitation region M times without saturation (or an enhancement cavity increases the intracavity power by B), **show** that the deposited power scales linearly: $(dQ/dt) = M\,(dQ/dt)_{\text{single}}$ (or B times, respectively), provided mode-matching maximizes overlap with the beam.

Solution

Absorption events ∝ local photon flux × path length. Multipass increases interaction length by M, while a build-up cavity increases photon flux by B. Since each excitation adds $h\nu$, the total dQ/dt scales linearly with M (or B).

Answer: $\boxed{(dQ/dt) \propto M \text{ or } B}$.

C) Qualitative / Descriptive (5)

Q1. When and why optothermal beats LIF and PAS

Solution (steps)

1. **Molecular beam**: collisions are absent → PAS (which needs collisional thermalization) fails.
2. **IR rovibrational levels**: very long radiative lifetimes; excited molecules can carry $h\nu$ to the bolometer.
3. **LIF in IR**: poor detector quantum efficiency, long lifetimes → weak fluorescence before molecules leave the view.
4. **Answer:** Optothermal is ideal for IR rovibrational spectroscopy **in beams**: collision-free transport of internal energy to an ultrasensitive, cryogenic bolometer.

Q2. Why operate near 1.5 K and use sapphire/diamond spreaders?

Solution (steps)

- **Sensitivity:** $\Delta T \propto 1/G$; but $\tau = C/G$. Lowering **both** C and G at cryogenic T raises ΔT while keeping τ manageable.
- **Materials:** Debye law $C \propto T^3$ → sapphire/diamond have tiny heat capacities at 1.5 K; they enlarge the capture area with negligible C penalty.
- **Answer:** Cryogenic operation minimizes C (and G); low-C spreaders boost intercepted flux without spoiling time response.

Q3. Chopping & lock-in: picking the right frequency

Solution (steps)

- The bolometer is a first-order low-pass with corner $\Omega_c = 1/\tau$.
- For flat response and maximum SNR, choose $f_{\text{chop}} \ll 1/(2\pi\tau)$ (practically $\tau \lesssim 0.1/f_{\text{chop}}$).
- Then the synchronous lock-in largely rejects $1/f$ drifts and ambient noise.
- **Answer:** Drive slow compared to τ^{-1} so the temperature can follow the modulation and lock-in can average down noise.

Q4. Practical noise/offsets and mitigation

Solution (steps)

- **Radiative loading** from warm walls → cold apertures, radiation shields, low-emissivity baffles.
- **Mechanical & electrical noise** → vibration isolation, shielded preamps, narrow lock-in bandwidth.
- **Laser scatter** heating solid parts → beam dumps, blackening, careful aperture placement.
- **Cavity drift** in enhancement setups → piezo locking and mode-matching.
- **Answer:** Thermal shielding + optical hygiene + narrowband detection stabilize baselines and push sensitivity.

Q5. Photothermal surface deflection (qualitative mechanism)

Solution (steps)

- A pulsed pump locally heats a spot on a solid; a thermal wave and thermoelastic bulge form.
- A weak probe beam (e.g., He-Ne) reflects; the surface tilt modulates the probe deflection vs time.
- Scanning pump wavelength across an adsorbate's absorption changes deposited energy → deflection amplitude/time-course encode adsorption and desorption.
- **Answer:** Time-resolved probe-beam deflection converts tiny, localized photothermal expansions into spectra and kinetics of surface-bound species.

(Optional) Instructor tips

- Pair **N1 & N5** to motivate enhancement cavities/multipass cells for threshold-limited experiments.
- Use **A2 & N3** together to emphasize the $(1+\Omega^2\tau^2)^{-1/2}$ roll-off and practical chopping choices.
- **A4** ties directly to the sapphire/diamond plate design (Fig. 1.32) and why it helps without hurting C.

Chapter 1.4

Problems

Problem Set — §1.4 Ionization Spectroscopy

Useful relations (from the section):

- Absorption (first step): $n_a = N_i\, n_{L1}\, \sigma_{ik}\, \Delta x$ (photons s^{-1})
- Ion rate (two-step): $S_I = N_i\, n_{L1}\, \sigma_{ik}\, \Delta x\, \frac{P_{kI}}{P_{kI}+R_k}\, \delta\, \eta$, with $P_{kI} = \sigma_{kI}\, n_{L2}$
- Maximal ion rate (ideal): $S_I^{\max} = n_a$ (when $\delta = \eta = 1$ and $P_{kI} \gg R_k$)
- Field ionization (Stark lowering; as given in text): $\displaystyle IP_{\rm eff}=IP-\sqrt{\frac{Z_{\rm eff}^3 E_0}{\pi\varepsilon_0}}$
- Thermionic diode: $\Delta i = e\, M\, N$ with $M=\Delta t_{\rm ion}/\Delta t_{\rm el}$

A) Numerical (5)

N1. Ion rate with finite ionization probability

Given: $N_i = 5.0 \times 10^{8}$ cm^{-3}, $\sigma_{ik} = 2.0 \times 10^{-17}$ cm^2, $\Delta x = 1.0$ cm.

Excitation laser: $P_1 = 2.0$ mW at $\lambda_1 = 500$ nm.

Ionizing step: $\sigma_{kI} = 1.0 \times 10^{-17}$ cm^2, flux density $n_{L2} = 1.0 \times 10^{24}$ cm^{-2}s^{-1}.

Upper-level relaxation $R_k = 1.0 \times 10^{8}$ s^{-1}.

Collection $\delta = 0.80$, detector $\eta = 0.90$. Compute S_I.

Step-by-step

1. Photon energy at 500 nm: $h\nu_1 = hc/\lambda_1 = (6.626 \times 10^{-34})(3.00 \times 10^{8})/(5.00 \times 10^{-7}) = 3.98 \times 10^{-19}$ J.
2. Photon rate $n_{L1} = P_1/h\nu_1 = 2.0 \times 10^{-3}/(3.98 \times 10^{-19}) = 5.03 \times 10^{15}$ s^{-1}.
3. First-step absorption rate:
4. $\sigma_{ik}\Delta x = 2.0 \times 10^{-17} \times 1.0 = 2.0 \times 10^{-17}$ cm^3.

5. $N_i(\sigma_{ik}\Delta x) = 5.0 \times 10^8 \times 2.0 \times 10^{-17} = 1.0 \times 10^{-8}$.
6. So $n_a = n_{L1} \times 1.0 \times 10^{-8} = 5.03 \times 10^7$ s^{-1}.
7. Ionization rate of $|k\rangle$: $P_{kI} = \sigma_{kI} n_{L2} = 1.0 \times 10^{-17} \times 1.0 \times 10^{24} = 1.0 \times 10^7$ s^{-1}.
8. Fraction surviving for ionization: $\frac{P_{kI}}{P_{kI}+R_k} = \frac{1.0\times10^7}{1.0\times10^7+1.0\times10^8} = 0.0909$.
9. Detection/collection: $\delta\eta = 0.80 \times 0.90 = 0.72$.
10. Ion rate: $S_I = n_a \times 0.0909 \times 0.72 = 5.03 \times 10^7 \times 0.06545 \approx 3.29 \times 10^6$ s^{-1}.

Answer: $\boxed{S_I \approx 3.3 \times 10^6 \text{ ions s}^{-1}}$.

N2. Required ionizing flux for 90% of the maximum rate

Target $S_I = 0.90\,(\delta\eta)\,n_a$. Show the required n_{L2} and evaluate for $\sigma_{kI} = 1.0 \times 10^{-17}$ cm^2, $R_k = 1.0 \times 10^8$ s^{-1}.

Step-by-step

1. From $S_I/n_a = (\delta\eta)\frac{P_{kI}}{P_{kI}+R_k}$. For the bracket to be 0.90 we need
2. $\frac{P_{kI}}{P_{kI}+R_k} = 0.90 \Rightarrow P_{kI} = 9\,R_k$.
3. Since $P_{kI} = \sigma_{kI} n_{L2}$,
4. $n_{L2}^{(90\%)} = \frac{9\,R_k}{\sigma_{kI}}$.
5. Numbers: $n_{L2} = \frac{9\times10^8}{1.0\times10^{-17}} = 9.0 \times 10^{25}$ cm^{-2}s^{-1}.

Answer: $\boxed{n_{L2} = 9.0 \times 10^{25} \text{ cm}^{-2}\text{s}^{-1}}$ for 90% of the maximum (before $\delta\eta$).

N3. Field needed for different detunings from the ionization limit

Example 1.15 quotes $\Delta IP = 10$ meV $\Rightarrow E_0 \simeq 1.7 \times 10^4$ V/m. Using the $\Delta IP \propto \sqrt{E_0}$ relation in Eq. (1.46) (hence $E_0 \propto (\Delta IP)^2$), find the field for $\Delta IP = 25$ meV.

Step-by-step

$$\frac{E_0(25)}{E_0(10)} = \left(\frac{25}{10}\right)^2 = 6.25 \;\Rightarrow\; E_0(25) = 6.25 \times 1.7 \times 10^4 = 1.06 \times 10^5 \text{ V/m}.$$

Answer: $\boxed{E_0 \approx 1.1 \times 10^5 \text{ V/m}}$.

N4. Pulsed ionization: do we beat R_k?

KrF excimer pulse: energy $E_p = 50$ mJ at $\lambda_2 = 248$ nm, duration $\Delta T = 10$ ns, beam area $A = 0.010$ cm^2. With $\sigma_{kI} = 1.0 \times 10^{-17}$ cm^2 and $R_k = 1.0 \times 10^8$ s^{-1}, evaluate P_{kI} and compare to R_k.

Step-by-step

1. Photon energy: $h\nu_2 = hc/\lambda_2 = (6.626 \times 10^{-34})(3.00 \times 10^8)/(2.48 \times 10^{-7}) = 8.02 \times 10^{-19}$ J.
2. Photons per pulse: $N_\gamma = E_p/h\nu_2 = 0.050/8.02 \times 10^{-19} = 6.23 \times 10^{16}$.
3. Photon flux density during pulse:
4. $n_{L2} = N_\gamma/(\Delta T\, A) = 6.23 \times 10^{16}/(1.0 \times 10^{-8} \times 0.010) = 6.23 \times 10^{26}$ cm^{-2}s^{-1}.
5. Ionization rate: $P_{kI} = \sigma_{kI} n_{L2} = 1.0 \times 10^{-17} \times 6.23 \times 10^{26} = 6.23 \times 10^9$ s^{-1}.
6. Compare: $P_{kI}/R_k = 6.23 \times 10^9/10^8 = 62.3 \gg 1$ → effectively saturates ionization during pulse.

Answer: $\boxed{P_{kI} \approx 6.2 \times 10^9 \text{ s}^{-1}\ (> 60 \times R_k)}$: pulsed ionization readily outpaces relaxation.

N5. Thermionic diode signal magnitude

A thermionic diode (space-charge limited) has magnification $M = 5.0 \times 10^4$. Laser excitation yields $N = 3.0 \times 10^3$ Rydberg ions s^{-1} in the space-charge zone. What current increase Δi is expected?

Step-by-step

$$\Delta i = eMN = (1.602 \times 10^{-19})\,(5.0 \times 10^{4})\,(3.0 \times 10^{3}) = 1.602 \times 10^{-19} \times 1.5 \times 10^{8}$$
$$= 2.40 \times 10^{-11}\ \text{A}.$$

Answer: $\boxed{\Delta i \approx 24\ \text{pA}}$.

B) Analytical / Symbolic (5)

A1. Fraction of the maximal ion rate & required n_{L2}

Task. Show that $\frac{S_I}{(\delta\eta)\,n_a} = \frac{P_{kI}}{P_{kI}+R_k} = \frac{\sigma_{kI} n_{L2}}{\sigma_{kI} n_{L2}+R_k}$.

For a desired fraction $f \in (0,1)$, solve the required n_{L2}.

Solution

From the given S_I, divide by $(\delta\eta)\,n_a$ to obtain the rational form in P_{kI}. Set $\frac{P_{kI}}{P_{kI}+R_k} = f \Rightarrow P_{kI} = \frac{f}{1-f} R_k$. Using $P_{kI} = \sigma_{kI} n_{L2}$ gives

$$\boxed{n_{L2} = \frac{f}{1-f}\,\frac{R_k}{\sigma_{kI}}}.$$

A2. Duty-cycle limit in a continuous molecular beam (pulsed lasers)

Task. In a continuous beam (speed $\bar{v}$), with a round laser spot of diameter D and laser repetition rate f_L, show that the **maximum** fraction of molecules that can be addressed (even with 100% in-pulse ionization) is $F = \min(1,\ f_L D/\bar{v})$.

Solution

Time a molecule spends inside the laser sheet $\approx D/\bar{v}$. Between pulses the dark time is $1/f_L$. A given molecule is "sampled" if a pulse occurs while it is inside the sheet. The sampling probability per transit $\approx$ (pulse rate)×(dwell time) $= f_L D/\bar{v}$, capped at 1. Hence

$$\boxed{F = \min\left(1,\ \frac{f_L D}{\bar{v}}\right)}.$$

A3. Two-color cw RTPI: beam-overlap strategy

Task. With Gaussian beams $I_1(\rho) = I_{1,0}e^{-2\rho^2/w_1^2}$ and $I_2(\rho) = I_{2,0}e^{-2\rho^2/w_2^2}$, first step near saturation ($I_1\gtrsim I_{\rm sat}$). Show that maximizing $\int I_2(\rho)\,[1-e^{-I_1(\rho)/I_{\rm sat}}]\ dA$ is achieved when the **peak** of I_2 sits on the **slope** of I_1 (as in Fig. 1.39), not necessarily at its center.

Solution (outline)

Write the functional $F=\int I_2(\rho)\,[1-e^{-I_1(\rho)/I_{\rm sat}}]\ dA$. Where $I_1\!\gg\!I_{\rm sat}$, the bracket saturates $\to 1$, giving little benefit from additional I_2. Maximal marginal gain occurs where $\partial[1-e^{-I_1/I_{\rm sat}}]/\partial I_1$ is largest, i.e. where $I_1\sim I_{\rm sat}$ (the slope). Placing the I_2 peak there maximizes the integrand. Thus the optimal lateral offset aligns the I_2 maximum with the I_1 slope.

Answer: $\boxed{\text{Offset }I_2 \text{ so its peak lies on the } I_1\sim I_{\rm sat} \text{ annulus (slope region).}}$

A4. Field for a desired barrier-lowering (symbolic)

Task. From $IP_{\rm eff}=IP-\sqrt{Z_{\rm eff}^3E_0/(\pi\varepsilon_0)}$, define $\Delta IP\equiv IP-IP_{\rm eff}$. Solve for $E_0(\Delta IP)$.

Solution

$\Delta IP=\sqrt{Z_{\rm eff}^3E_0/(\pi\varepsilon_0)}\Rightarrow E_0=(\pi\varepsilon_0/Z_{\rm eff}^3)\,(\Delta IP)^2$.

Answer: $\boxed{E_0=\dfrac{\pi\varepsilon_0}{Z_{\rm eff}^3}\,(\Delta IP)^2}$.

A5. Minimum detectable density with sub-unity detection fraction

Task. If only a fraction $f_{\rm det}\equiv(\delta\eta)\,\dfrac{P_{kI}}{P_{kI}+R_k}$ of absorbed photons yield counted ions, generalize

$N_i^{\min} = \frac{1}{n_{L1}\sigma_{ik}L}$ to include $f_{\rm det}$.

Solution

Set the "one counted ion per second" condition: $S_I=f_{\rm det}\,n_a\ge1\ \text{s}^{-1}$. Using $n_a = N_i n_{L1} \sigma_{ik} L$, get

$$\boxed{N_i^{\min}=\frac{1}{f_{\rm det}\,n_{L1}\,\sigma_{ik}\,L}}.$$

C) Qualitative / Descriptive (5)

Q1. REMPI vs non-resonant two-photon ionization (2P)

Step-wise answer

1. **Cross-section:** REMPI leverages real intermediate levels → orders-of-magnitude larger effective cross sections than non-resonant 2P.
2. **Selectivity:** REMPI is state/rotationally selective (and parity-selective for appropriate schemes), enabling species/isotope selectivity.
3. **Power needs:** Non-resonant 2P demands far higher intensities (pulsed lasers).
4. **When use non-resonant:** If no suitable resonances exist or to avoid intermediate-state dynamics.

Q2. Autoionizing Rydberg levels for efficient ionization

Step-wise answer

1. **Mechanism:** Excite $|k\rangle$ → high Rydberg above threshold → autoionization to $M^+ + e^-$.
2. **Why efficient:** Bound–bound cross sections to Rydberg series are large; autoionization proceeds rapidly.
3. **Experimental pay-off:** Much lower n_{L2} needed than direct bound–free; helps with cw ionization and reduces focusing demands.

Q3. Pulsed vs cw lasers in RTPI: pros, cons, and fixes

Step-wise answer

1. **Pulsed:** Huge instantaneous $n_{L2} \rightarrow P_{kI} \gg R_k$ during pulse; cons: broad bandwidth; tiny duty cycle.
2. **Continuous beams:** Duty-cycle loss $F \sim f_L D/\bar{v}$ (A2).
3. **Mitigations:** Use pulsed molecular beams timed to laser; or counter-/co-propagating geometry to increase re-sampling; use high-rep-rate sources (e.g., Cu-vapor-pumped dye).
4. **CW:** Narrow linewidth, 100% duty cycle but lower intensity; rely on tight focusing and autoionizing transitions.

Q4. RTPI + mass spectrometry for isotope-selective spectra

Step-wise answer

1. **Double discrimination:** Laser wavelength selects the species/state; MS selects mass → separates overlapping optical spectra.
2. **TOF with pulsed lasers:** Parallel acquisition of many masses per shot; timing resolution gives clean separation.
3. **Quadrupole with cw:** Sequential mass selection; lower throughput but compatible with cw excitation.
4. **Applications:** Isotope shifts/abundances, cluster distributions, gentle laser desorption for fragile biomolecules.

Q5. Thermionic diode (optogalvanic-type) detection: why so sensitive?

Step-wise answer

1. **Space-charge region:** Laser creates ions near cathode; each ion neutralizes space charge for time $\Delta t_{\rm ion}$.
2. **Magnification:** During $\Delta t_{\rm ion}$, $n=\Delta t_{\rm ion}/\Delta t_{\rm el}=M$ extra electrons escape → current gain $\Delta i = eMN$.

3. **Design notes:** Nearly field-free excitation zone minimizes Stark shifts; large M (up to 10^5) yields pA-level sensitivity to tiny ion rates.

(Instructor tips)

- Use **N2** and **A1** together to show how to engineer n_{L2} for a desired fraction of the max rate.
- Pair **N4** with **Q3** to discuss why pulsed sources crush R_k but suffer duty-cycle penalties.
- Use **A5** to generalize detection limits when $\delta\eta < 1$ and $P_{kI} \gg / R_k$.

Chapter 1.5

Problems

Problem Set — §1.5 Optogalvanic Spectroscopy

Useful relations from the section:

- Optogalvanic signal (schematic form):

  $\Delta U = R\,\Delta I = a[\Delta n_i\, IP(E_i) - \Delta n_k\, IP(E_k)]$

  where a summarizes discharge geometry, volume fraction, charge balance, etc., Δn_j are laser-induced population changes, and $IP(E_j)$ are effective ionization probabilities from level E_j.

- Lock-in transfer for a first-order RC readout at angular frequency ω: amplitude factor $1/\sqrt{1+(\omega RC)^2}$.

- Intracavity placement boosts field intensity by $\sim q = 1/T_2$ (Sect. 1.2.3), giving $\Delta U_{\text{intra}} \approx q\,\Delta U_{\text{single}}$.

- Wavenumber/frequency conversion: $\nu\,[\text{Hz}] = c\,[\text{cm/s}] \times \tilde{\nu}\,[\text{cm}^{-1}]$.

A) Numerical (5)

N1. Predicting the signal magnitude

A hollow-cathode discharge is monitored with series resistor $R = 10\,\text{k}\Omega$. Laser pumping on $E_i \rightarrow E_k$ produces $\Delta n_i = +2.0 \times 10^9\,\text{cm}^{-3}$ and $\Delta n_k = -0.5 \times 10^9\,\text{cm}^{-3}$ within the illuminated sub-volume. With effective ionization probabilities $IP(E_i) = 3.0 \times 10^{-7}\,\text{cm}^3\text{s}^{-1}$, $IP(E_k) = 1.0 \times 10^{-6}\,\text{cm}^3\text{s}^{-1}$ and proportionality $a = 2.0 \times 10^{-12}\,\text{A cm}^3$ (lumps geometry and fraction of discharge sampled), compute ΔU.

Solution

$\Delta I = a\,[\Delta n_i IP(E_i) - \Delta n_k IP(E_k)] = 2.0 \times 10^{-12}[(2.0 \times 10^9)(3.0 \times 10^{-7}) - (-0.5 \times 10^9)(1.0 \times 10^{-6})]$

Bracket: $0.6 + 0.5 = 1.1\ \text{s}^{-1}$. Thus $\Delta I = 2.2 \times 10^{-12}$ A.

$\Delta U = R\Delta I = 10^4 \times 2.2 \times 10^{-12} = 2.2 \times 10^{-8}$ V $= 22$ nV.

Answer: $\boxed{\Delta U \approx 22 \text{ nV}}$ (tiny, hence lock-in averaging is essential).

N2. SNR and averaging time with a lock-in

Signal amplitude is $\Delta U = 0.50\,\mu$V at the chopper frequency. Input-referred noise density is $e_n = 5$ nV/$\sqrt{\text{Hz}}$. With a lock-in equivalent noise bandwidth ENBW $\approx 1/(4\tau)$, what integration time τ is needed for SNR $= 10$?

Solution

Noise RMS $= e_n\sqrt{\text{ENBW}} = e_n\sqrt{1/(4\tau)}$.

SNR $= \Delta U/\left(e_n/2\sqrt{\tau}\right) = 2\Delta U\sqrt{\tau}/e_n$.

Set $10 = 2(0.5 \times 10^{-6})\sqrt{\tau}/(5 \times 10^{-9}) \Rightarrow 10 = (0.2)\sqrt{\tau}$.

$\sqrt{\tau} = 50 \Rightarrow \tau = 2500$ s ≈ 42 min.

Answer: $\boxed{\tau \approx 2.5 \times 10^3 \text{ s}}$.

N3. Uranium/Thorium as wavelength markers: frequency accuracy

Reference lines provide ± 0.001 cm^{-1} absolute accuracy. Convert this to MHz at $\lambda = 600$ nm.

Solution

1 cm$^{-1} \rightarrow c = 2.99792458 \times 10^{10}$ Hz.

Thus 0.001 cm$^{-1} \rightarrow 2.9979 \times 10^7$ Hz ≈ 30 MHz.

Answer: $\boxed{\sim 30 \text{ MHz}}$ absolute frequency accuracy per marker.

N4. Intracavity boost

Single-pass optogalvanic signal is $\Delta U_{sp} = 0.20$ mV. Placing the discharge inside an external enhancement cavity with output mirror $T_2 = 0.02$ (thus $q = 1/T_2 = 50$) and negligible extra loss, estimate ΔU.

Solution

$\Delta U \approx q\,\Delta U_{sp} = 50 \times 0.20$ mV $= 10$ mV.

Answer: $\boxed{10 \text{ mV}}$.

N5. Choosing the chopper frequency with RC readout

Readout has $R = 10\,\text{k}\Omega$ and $C = 1.0\,\mu$F. For sinusoidal modulation, amplitude is reduced by $1/\sqrt{1+(\omega RC)^2}$. What is the modulation frequency f where the amplitude is 90% of DC?

Solution

Set $1/\sqrt{1+(\omega RC)^2} = 0.9 \Rightarrow (\omega RC)^2 = (1/0.9^2) - 1 \approx 0.2346$.

$\omega RC = \sqrt{0.2346} = 0.484 \Rightarrow \omega = 0.484/(10^4 \times 10^{-6}) = 48.4$ rad/s.

$f = \omega/2\pi \approx 7.7$ Hz.

Answer: $\boxed{f \approx 7.7 \text{ Hz}}$ (go higher only if noise falls faster than the RC roll-off).

B) Analytical / Symbolic (5)

A1. Signal polarity conditions

Show when ΔU is positive or negative upon pumping $E_i \rightarrow E_k$.

Solution

$$\Delta U \propto \Delta n_i\, IP(E_i) - \Delta n_k\, IP(E_k).$$

Optical pumping depletes $E_i \Rightarrow \Delta n_i < 0$, and populates $E_k \Rightarrow \Delta n_k > 0$.

If $IP(E_k) \gg IP(E_i)$, second term dominates $\Rightarrow \Delta U < 0$.

If $IP(E_i)$ is much larger (e.g., E_i is a metastable with high collisional ionization), then $|\Delta n_i|\, IP(E_i)$ can dominate ⇒ $\Delta U > 0$.

Answer: \boxed{\Delta U>0 if $|\Delta n_i|\, IP(E_i) > \Delta n_k\, IP(E_k)$; otherwise $\Delta U < 0$.}

A2. Intracavity enhancement of the optogalvanic signal

Assuming $\Delta U \propto$ absorbed photon rate and intracavity intensity is q times higher, show $\Delta U_{\text{intra}} \approx q\, \Delta U_{\text{single}}$ (no saturation).

Solution

Weak absorption, linear regime: population perturbations $\Delta n_j \propto I$. Inside cavity $I \to qI$, thus $\Delta n_j \to q\, \Delta n_j$. Since $IP(E_j)$ are discharge properties,

$$\Delta U \to a[q\Delta n_i IP(E_i) - q\Delta n_k IP(E_k)] = q\, \Delta U.$$

Answer: $\boxed{\Delta U_{\text{intra}} \simeq q\, \Delta U_{\text{single}}}$ (until saturation/space-charge effects appear).

A3. RC and lock-in optimization

Given white detector noise and $1/f$ technical noise that rolls off above f_c, argue the optimal modulation frequency $f_m \sim \max(f_c,\, 1/2\pi RC)$.

Solution

Signal transfer $|H(\omega)| = 1/\sqrt{1 + (\omega RC)^2}$ penalizes high f; noise spectral density falls above f_c. SNR $\propto |H(\omega)|/\sqrt{S_n(\omega)}$ is maximized near the knee where S_n is low but $|H|$ still close to unity: pick $f_m \gtrsim f_c$ yet $\omega RC \lesssim 1 \Rightarrow f_m \lesssim 1/2\pi RC$. Jointly, $f_m \sim \max(f_c, 1/2\pi RC)$.

Answer: $\boxed{f_m \approx \max(f_c,\, 1/2\pi RC)}$.

A4. Extended ionization channels

If multiple ionization paths exist with rates $IP_j^{(p)}$ (electron impact), $IP_j^{(m)}$ (metastable collisions), and $IP_j^{(\gamma)}$ (direct photoionization), show that

$$\Delta U = a \sum_{j\in\{i,k\}} \left[\Delta n_j \underbrace{\left(IP_j^{(p)} + IP_j^{(m)} + IP_j^{(\gamma)} \right)}_{IP_{\text{eff}}(E_j)} \right] \times s_j$$

with $s_i = +1$, $s_k = -1$.

Solution

Total ionization probability from level E_j is the sum of competing channels in the linear regime; insert into base expression and keep signs for i, k.

Answer: $\boxed{\text{Replace } IP(E_j) \rightarrow IP_{\text{eff}}(E_j) = \sum\text{channels},\ \ s_i = +1, s_k = -1.}$

A5. Wavenumber marker accuracy → wavelength accuracy

Derive $\delta\lambda$ from $\delta\tilde{\nu}$ at wavelength λ. (Useful for calibrations.)

Solution

$\tilde{\nu} = 1/\lambda$ (with λ in cm). Differentiate: $d\tilde{\nu} = -d\lambda/\lambda^2$. Hence $|\delta\lambda| = \lambda^2\, \delta\tilde{\nu}$ (consistent units). For λ in cm, convert to nm if needed.

Answer: $\boxed{\delta\lambda = \lambda^2\, \delta\tilde{\nu}}$ (use consistent units).

C) Qualitative / Conceptual (5)

Q1. Why optogalvanic over direct absorption/LIF in discharges?

Solution (key points)

1. **High sensitivity** to absorbed photons via current change; avoids "small difference of two large numbers."
2. **Simple hardware** (a resistor and lock-in) and works in glowing plasmas where optics is challenging.
3. **Access to states** populated by electron impact (incl. ions, radicals); LIF may be weak or spectrally congested.

Q2. Why can the signal flip sign?

Solution (key points)

- Pumping depletes E_i (reduces its ionization contribution) and fills E_k (increases its contribution).
- Net sign follows which level's ionization probability dominates after pumping (A1).
- Changes in electron temperature can further tilt the balance.

Q3. Role of hollow cathodes and discharge current

Solution (key points)

- **Sputtering**: higher current → more cathode material atoms/ions in plasma → many metal lines appear (Fig. 1.44).
- Hollow-cathode geometry enhances path length and excitation → stronger signals.
- Buffer gas choice/pressure set collision and ionization balance.

Q4. Why excimers are ideal targets?

Solution (key points)

- Species like He$_2^*$, H$_2^*$ exist **only** in excited states; discharges populate them.
- Optogalvanic detection is natural, since optical pumping perturbs ionization/electron balance even without ground-state population.

Q5. Practical tips to maximize SNR

Solution (key points)

- Use **lock-in** at a frequency above technical noise but below RC cutoff (A3).
- Minimize optical scatter; stabilize discharge; shield electronics.
- Consider **intracavity** boost (A2) or **thermionic diode** space-charge amplification when compatible.
- For calibration, **split** a fraction of the laser into a Th/U hollow-cathode lamp to get dense, accurate markers (~0.001 cm^{-1}).

Chapter 1.6

Problems

Problem Set — §1.6 Velocity-Modulation Spectroscopy (VMS)

Core relations & ideas from the section

- Ion drift gives a Doppler shift: $\Delta\omega = \mathbf{k} \cdot \mathbf{v_D}$.
- With beam collinear to drift, $\Delta\omega = k v_D$ with $k = 2\pi/\lambda$.
- In frequency units: $\Delta\nu = v_D/\lambda$.
- In wavenumber: $\Delta\tilde{\nu} = \Delta\nu/c = (v_D/c) \cdot (1/\lambda) = (v_D/c)\,\tilde{\nu}$.
- AC field $E(t) = E_0 \cos\Omega t \Rightarrow v_D(t) = \mu E(t)$ (mobility μ) ⇒ **frequency modulation** of the ion line: $\nu(t) = \nu_0 + \Delta\nu_{\text{pk}} \cos\Omega t$, $\Delta\nu_{\text{pk}} = \mu E_0/\lambda$.
- Lock-in at Ω yields **1st-derivative line shape** for ions; neutrals (no drift) give ~no signal at Ω. Positive vs negative ions show **opposite phase**.

A) Numerical (5)

N1. Drift-induced Doppler shift (MHz)

A positive ion in a discharge has mobility $\mu = 1.5\ \text{cm}^2\,\text{V}^{-1}\,\text{s}^{-1} = 1.5 \times 10^{-4}\ \text{m}^2\,\text{V}^{-1}\,\text{s}^{-1}$. An AC field has peak amplitude $E_0 = 3.0 \times 10^4\ \text{V}\,\text{m}^{-1}$. For an IR transition at $\lambda = 3.00\ \mu\text{m}$, compute the **peak** frequency deviation $\Delta\nu_{\text{pk}}$ (in MHz).

Step-by-step

1. Peak drift speed: $v_D^{\text{pk}} = \mu E_0 = (1.5 \times 10^{-4})(3.0 \times 10^4) = 4.5\ \text{m}\,\text{s}^{-1}$.
2. Frequency deviation: $\Delta\nu_{\text{pk}} = v_D^{\text{pk}}/\lambda = 4.5/(3.00 \times 10^{-6}) = 1.5 \times 10^6\ \text{Hz} = 1.5\ \text{MHz}$.

Answer: $\boxed{1.5\ \text{MHz}}$.

N2. Required field for a target deviation

You want $\Delta\nu_{\text{pk}} = 5.0$ MHz at $\lambda = 632.8$ nm (HeNe probe). The ion mobility is $\mu = 1.0\ \text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1} = 1.0 \times 10^{-4}\ \text{m}^2\ \text{V}^{-1}\ \text{s}^{-1}$. What E_0 is required?

Step-by-step

$$\Delta\nu_{\text{pk}} = \frac{\mu E_0}{\lambda} \Rightarrow E_0 = \frac{\Delta\nu_{\text{pk}}\lambda}{\mu}.$$

Insert values: $E_0 = (5.0 \times 10^6)(6.328 \times 10^{-7})/(1.0 \times 10^{-4})$.

Compute numerator: $5.0 \times 10^6 \cdot 6.328 \times 10^{-7} = 3.164$. Divide by $1.0 \times 10^{-4} \Rightarrow 3.164 \times 10^4\ \text{V m}^{-1}$.

Answer: $\boxed{E_0 \approx 3.16 \times 10^4\ \text{V/m}}$.

N3. 1st-harmonic amplitude vs linewidth (Lorentzian)

A Lorentzian absorbance profile (peak absorbance A_0, HWHM Γ in Hz) is driven by small FM: $\nu(t) = \nu_0 + \Delta\nu_{\text{pk}}\cos\Omega t$ with $\Delta\nu_{\text{pk}} \ll \Gamma$. Show numerically how big the **1st-harmonic** (lock-in) absorbance is at line center if $A_0 = 2.0 \times 10^{-3}$, $\Gamma = 80$ MHz, $\Delta\nu_{\text{pk}} = 2.0$ MHz.

Step-by-step

1. Small-FM expansion: $A(\nu_0 + \delta) \approx A(\nu_0) + A'(\nu_0)\delta$. The 1st-harmonic amplitude at Ω is $A_1 = |A'(\nu_0)|\,\Delta\nu_{\text{pk}}$.

2. For Lorentzian $A(\nu) = A_0/\left[1 + \left((\nu - \nu_c)/\Gamma\right)^2\right]$. Derivative:

$$A'(\nu) = A_0 \cdot \frac{-2(\nu - \nu_c)}{\Gamma^2} \cdot \frac{1}{[1 + \left((\nu - \nu_c)/\Gamma\right)^2]^2}.$$

At $\nu_0 = \nu_c$ (line center), $A'(\nu_0) = 0 \Rightarrow$ the **in-phase** 1st-harmonic at exact center is zero; the dispersive signal crosses through zero there.

3) Practical amplitude near $|\nu - \nu_c| = \Gamma/\sqrt{3}$ (slope maximum). Evaluate $|A'|_{\max} = \left(3\sqrt{3}/8\right) A_0/\Gamma$ (standard result for Lorentzian slope).

4) Compute: $|A'|_{\max} \approx \left(3\sqrt{3}/8\right)(2.0 \times 10^{-3})/(80 \times 10^6)$.

$(3\sqrt{3}/8) \approx 0.6495$. So $|A'|_{\max} \approx 0.6495 \times 2.0 \times 10^{-3}/8.0 \times 10^{7} \approx 1.62 \times 10^{-11}\ \mathrm{Hz}^{-1}$.

5) Then $A_{1,\max} \approx |A'|_{\max} \Delta\nu_{\mathrm{pk}} = 1.62 \times 10^{-11} \times 2.0 \times 10^{6} \approx 3.2 \times 10^{-5}$.

Answer: Dispersive 1st-harmonic is **zero at center** and peaks at $\sim 3 \times 10^{-5}$ absorbance near the slope maximum for these parameters.

N4. Picking the modulation frequency (transit & RC)

Cell length $L = 4$ cm. Ion mobility $\mu = 2.0\ \mathrm{cm^2\,V^{-1}\,s^{-1}}$. Peak voltage $V_0 = 200$ V across the length (approx uniform field). (i) Compute peak drift speed. (ii) If the lock-in operates best for $\Omega/2\pi$ between 1 and 30 kHz and your detection RC corner is $f_c = 20$ kHz, pick a reasonable modulation frequency ensuring ions can follow the field.

Step-by-step

(i) Field $E_0 = V_0/L = 200/0.04 = 5000\ \mathrm{V\,m^{-1}}$.

$\mu = 2.0\ \mathrm{cm^2/Vs} = 2.0 \times 10^{-4}\ \mathrm{m^2/Vs}$.

$v_D^{\mathrm{pk}} = \mu E_0 = 2.0 \times 10^{-4} \cdot 5.0 \times 10^{3} = 1.0\ \mathrm{m\,s^{-1}}$.

(ii) Ion momentum relaxation is typically fast in discharges; with $v_D \sim 1$ m/s, the ion responds quasi-statically up to many kHz. Choose f near/above the RC 1/f knee but $\leq f_c$: $f \approx 20$ kHz is a good choice.

Answer: (i) $\boxed{v_D^{\mathrm{pk}} \approx 1.0\ \mathrm{m/s}}$. (ii) $\boxed{f \approx 20\ \mathrm{kHz}}$.

N5. Opposite phases for ± ions (numerical phase check)

Reference the lock-in to the applied field $E(t) = E_0 \cos\Omega t$. For **positive ions**, $\Delta\nu(t) = +(\mu E_0/\lambda)\cos\Omega t$; for **negative ions**, $\Delta\nu(t) = -(\mu E_0/\lambda)\cos\Omega t$. What relative phase does the 1st-harmonic dispersive signal show?

Step-by-step

- The 1st-harmonic $S_1 \propto (dA/d\nu)\,\Delta\nu(t)$. The sign of $\Delta\nu(t)$ flips between ± ions.

- Therefore $S_{1,-} = -S_{1,+}$ at all detunings (assuming same $|\mu|$).
- Relative phase: **180°**.

Answer: Negative ions are 180° out of phase with positive ions (relative to E).

B) Analytical / Symbolic (5)

A1. Small-FM expansion → derivative signal

Let the absorbance be $A(\nu)$. With VMS, $\nu(t) = \nu_0 + \Delta\nu_{\text{pk}}\cos\Omega t$, $\Delta\nu_{\text{pk}} \ll$ linewidth. Show that the lock-in 1st-harmonic amplitude at ν_0 is $S_1(\nu_0) = 1/2\ A'(\nu_0)\,\Delta\nu_{\text{pk}}$ (up to an instrument gain).

Step-by-step

1. Taylor expand: $A[\nu(t)] = A(\nu_0) + A'(\nu_0)\Delta\nu_{\text{pk}}\cos\Omega t + 1/2\ A''(\nu_0)\Delta\nu_{\text{pk}}^2\cos^2\Omega t + \cdots$.
2. The component at Ω is the coefficient of $\cos\Omega t$ after orthogonal detection; $\cos^2\Omega t$ contributes only DC and 2Ω.
3. Using sinusoidal lock-in with 1× scaling, in-phase amplitude $S_1 = \frac{1}{2}A'(\nu_0)\Delta\nu_{\text{pk}}$ (the $1/2$ arises from RMS/phase-sensitive detection convention).

Answer: $S_1(\nu_0) \propto A'(\nu_0)\,\Delta\nu_{\text{pk}}$ (with the usual $1/2$ factor for sinusoidal reference).

A2. Why neutrals vanish at the modulation frequency

Assuming neutrals have negligible drift ($v_D \approx 0$), prove that their contribution to the Ω lock-in channel is ~zero to first order.

Step-by-step

- Their instantaneous frequency is $\nu(t) = \nu_0$ (no FM).
- Expand $A[\nu(t)]$: only DC term remains; no $\cos\Omega t$ component.

- Any residual at Ω must arise from secondary effects (e.g., Stark shifts, intensity modulation), typically suppressed compared to ion FM.

Answer: No 1st-harmonic term for neutrals in ideal VMS ⇒ they vanish at Ω.

A3. Opposite sign for cations vs anions

Show analytically that cations and anions produce derivative signals of opposite sign for a collinear probe, given the lock-in reference is the applied field.

Step-by-step

- For collinear geometry: $\Delta\nu(t) = \pm\mu E_0 \cos\Omega t/\lambda$ (plus for cations, minus for anions).
- 1st-harmonic $S_1 \propto A'(\nu_0)\Delta\nu(t)$.
- The ± enters multiplicatively, inverting S_1.

Answer: $S_{1,\text{anion}} = -S_{1,\text{cation}}$.

A4. Oblique beam angle dependence

If the probe makes angle θ with $\mathbf{v_D}$, show $\Delta\nu_{\text{pk}}(\theta) = \frac{\mu E_0}{\lambda}\cos\theta$. How would you exploit this to confirm an assignment?

Step-by-step

- Doppler shift: $\Delta\omega = \mathbf{k} \cdot \mathbf{v_D} = k v_D \cos\theta$.
- Divide by 2π: $\Delta\nu = v_D \cos\theta/\lambda = (\mu E_0/\lambda)\cos\theta$.
- Strategy: measure $S_1(\theta)$ and fit $\propto \cos\theta$; ions follow $\cos\theta$, neutrals stay ~flat (zero).

Answer: $\Delta\nu_{\text{pk}}(\theta) = (\mu E_0/\lambda)\cos\theta$; a $\cos\theta$ dependence verifies ionic origin.

A5. Wavenumber form of the shift

Derive $\Delta\tilde{\nu}$ (in cm^{-1}) in terms of v_D, $\tilde{\nu}$, and c.

Step-by-step

- $\nu = c\tilde{\nu} \Rightarrow \Delta\nu = c\,\Delta\tilde{\nu}$.
- First-order Doppler: $\Delta\nu = \nu(v_D/c) = (c\tilde{\nu})(v_D/c) = \tilde{\nu}\,v_D$.
- Therefore $\Delta\tilde{\nu} = \Delta\nu/c = \tilde{\nu}\,v_D/c$.

Answer: $\boxed{\Delta\tilde{\nu} = (v_D/c)\,\tilde{\nu}}$.

C) Qualitative / Conceptual (5)

Q1. Why VMS cleanly separates ions from neutrals

Step-by-step points

- Only ions acquire an **AC drift velocity**; neutrals don't ⇒ **FM only for ions**.
- Lock-in at the discharge modulation frequency detects the derivative of ionic lines and largely **rejects neutrals and background**.
- **Sign** of the dispersive signal reverses for cations vs anions (phase tag).

Answer: VMS gives a frequency-tag unique to ions, suppressing neutral congestion and enabling unambiguous assignments.

Q2. Benefit of high modulation frequencies (up to ~50 kHz)

Step-by-step points

- Moves detection above $1/f$ technical noise.
- Still well below electronic bandwidth; ions follow quasi-statically (high collision rates).
- Compatible with **lock-in** integration for high SNR.

Answer: Higher f boosts SNR by escaping flicker noise while keeping ionic response intact.

Q3. Why IR came first for VMS, then electronic bands

Step-by-step points

- Many ionic **vib-rot** transitions lie in the IR; **diode/color-center lasers** are agile/narrow.
- Discharge environments populate ionic rovibrational manifolds.
- Later, **dye lasers** enabled access to **electronic** bands with VMS.

Answer: Laser availability and line densities made IR a natural first playground; advances extended VMS to electronic transitions.

Q4. Practical pitfalls / false positives

Step-by-step points

- **Field inhomogeneity** or geometry can modulate intensity or Stark-shift neutrals slightly (residual signals).
- **Phase errors** if lock-in reference not strictly tied to field polarity.
- **Space-charge** or discharge instability can imprint extra AM/FM on the probe.

Answer: Careful electrode design, shielding, and phase referencing are key to preserve ion-only selectivity.

Q5. Compare VMS vs laser FM spectroscopy

Step-by-step points

- Both yield **derivative-like** detection and lock-in SNR gains.
- **FM spectroscopy** modulates the *source* frequency; **VMS** modulates the *absorber's rest frame* (via drift).

- VMS uniquely tags **charge sign** (phase) and **filters neutrals**.

Answer: Conceptually similar detection physics; VMS adds charge-selective tagging not available in source-FM methods.

1.7.1 Laser Magnetic Resonance (LMR)

Numerical (5)

N1. Zeeman tuning in Hz

A transition with $\Delta(gM) = g'M' - g''M'' = +1$ is probed at magnetic field $B = 0.120$ T. Compute the frequency shift.

Data: $\mu_B/h = 13.996$ GHz/T.

Solution.

$\Delta\nu = (\mu_B/h)\,\Delta(gM)\,B = 13.996 \times 1 \times 0.120 = 1.6795$ GHz.

Answer: $\boxed{1.68 \text{ GHz}}$.

N2. Zeeman tuning in wavenumber

Same as N1, but report $\Delta\tilde{\nu}$ in cm^{-1}.

Data: $\mu_B/(hc) = 0.4669\ \text{cm}^{-1}/\text{T}$.

Solution.

$\Delta\tilde{\nu} = \big(\mu_B/(hc)\big)\,\Delta(gM)\,B = 0.4669 \times 1 \times 0.120 = 0.0560\ \text{cm}^{-1}$.

Answer: $\boxed{5.60 \times 10^{-2}\ \text{cm}^{-1}}$.

N3. Field needed to hit a fixed laser line

A fixed FIR laser is at $\tilde{\nu}_L = \tilde{\nu}_0 + 0.80\ \mathrm{cm}^{-1}$ above the zero-field transition. With $\Delta(gM) = +2$, what B is required?

Solution.

$B = \Delta\tilde{\nu}/\left[\left(\mu_B/(hc)\right)\Delta(gM)\right] = 0.80/(0.4669 \times 2) = 0.857\ \mathrm{T}.$

Answer: $\boxed{0.86\ \mathrm{T}}$.

N4. Extracting g from slope

You measure a linear slope $dv/dB = 7.00\ \mathrm{GHz/T}$ for a branch with $M' = M'' + 1$ and $g'' \approx 0$. Estimate g'.

Solution.

$dv/dB = (\mu_B/h)(g'M' - g''M'') \simeq (\mu_B/h)g'M'.$

For $\Delta M = +1$ with typical $|M'| = 1$: $g' \simeq \frac{dv/dB}{(\mu_B/h)M'} = \frac{7.00}{13.996\times1} = 0.50.$

Answer: $\boxed{g' \approx 0.50 \text{ (for } M' = 1)}$.

N5. Modulation amplitude vs derivative signal

LMR uses small B-field modulation $B(t) = B_0 + B_1\cos\Omega t$. For a Lorentzian line with HWHM $\Gamma_B = 12\ \mathrm{mT}$ (in B units) and peak absorbance $A_0 = 2.0 \times 10^{-3}$, pick B_1 to maximize the 1st-harmonic response (small-modulation regime).

Solution.

Derivative detection is optimal for $B_1 \lesssim 0.3\,\Gamma_B$ (keeps linear FM).

$\Rightarrow B_1 \sim 0.3 \times 12\ \mathrm{mT} \approx 3.6\ \mathrm{mT}.$

Answer: $\boxed{B_1 \approx 3\text{–}4\ \mathrm{mT}}$.

Analytical (5)

A1. Zeeman tuning formula

Show $\omega = \omega_0 - (\mu_0/\hbar)(g'M' - g''M'')B$.

Solution.

Level shift: $E = E_0 - g\mu_0 BM$. Transition shift: $\Delta E = -(g'M' - g''M'')\mu_0 B$.

Divide by $\hbar$: $\Delta\omega = \Delta E/\hbar = -(\mu_0/\hbar)\Delta(gM)B$.

Hence $\omega = \omega_0 + \Delta\omega$. ✔

A2. Selection rules & polarization

Derive why $\Delta M = 0, \pm 1$ and how polarization selects them.

Solution.

Dipole matrix elements $\langle J'M' | \mathbf{d} \cdot \mathbf{e}_q | J''M'' \rangle$ with spherical components $q = 0, \pm 1$ enforce $\Delta M = q$.

Linear light ∥ B excites $q = 0$ (π transitions, $\Delta M = 0$); circular $\sigma^{\pm}$ (or linear $\perp B$) selects $q = \pm 1$ ($\Delta M = \pm 1$). ✔

A3. Dispersive line via B modulation

Show that small B-FM yields a 1st-derivative lineshape in B.

Solution.

$A\big(B(t)\big) \approx A(B_0) + A'(B_0)B_1 \cos\Omega t + \cdots$. Lock-in at Ω gives $\propto A'(B_0)$, i.e., derivative with respect to B. ✔

A4. Intracavity enhancement factor

If the sample is intracavity with output coupler transmission T_2 dominating losses, show the sensitivity scales as $q = 1/T_2$.

Solution.

Intracavity power $P_{\text{int}} = P_{\text{out}}/T_2 \Rightarrow$ absorption signal $\propto P_{\text{int}}$.

Thus enhancement $q = 1/T_2$. (Sect. 1.2.3.) ✔

A5. Faraday LMR signal

Explain how crossed polarizers + longitudinal B give resonance-only transmission.

Solution.

Near resonance, circular birefringence (Faraday effect) rotates the polarization by angle $\theta_F \propto$ dispersion. Crossed analyzer passes intensity $\propto \sin^2\theta_F$, negligible off-resonance. Modulating B yields derivative detection. ✔

Qualitative (5)

Q1. Why LMR is great for radicals

Unpaired electrons ⇒ large g, large Zeeman shifts ⇒ cm^{-1}-level tuning in 1–2 T, letting fixed lasers "scan" lines. Intracavity boosts sensitivity; detection at B-modulation suppresses intensity noise.

Q2. Phase tagging of $\Delta M = \pm 1$

With zero-field tuning, $\Delta M = +1$ and -1 resonances appear with opposite phase under B modulation, aiding assignment.

Q3. Voigt-geometry LMR

Transverse B, linear input at 45° to B: linear dichroism/birefringence (Voigt effect) rotates polarization only on resonance; analyzer passes signal, blocks background.

Q4. Tradeoffs of B strength

Stronger B: wider tuning but increased inhomogeneity, potential power broadening via longer dwell at detuning, and instrument limits (magnet stability).

Q5. Doppler-free LMR

Counterpropagating beams in the LMR cell produce Lamb dips at resonance; helps extract fine/hyperfine and collisional parameters precisely.

1.7.2 Stark Spectroscopy

We treat both **linear (first-order)** and **quadratic** (second-order) Stark responses by parameterizing the measured shift as

$\Delta\nu = S_1 E + S_2 E^2,$

where S_1 (Hz · m V^{-1}) encodes effective dipole-matrix differences for first-order cases and S_2 (Hz · m^2 V^{-2}) encodes differential polarizability for quadratic cases. Conversions: $1\ \mathrm{D} = 3.33564 \times 10^{-30}\ \mathrm{C\,m}$.

Numerical (5)

N6. Linear Stark slope → dipole (effective)

Measured slope: $d\nu/dE = 2.50\ \mathrm{MHz/(kV/cm)}$ for a $\Delta M = 0$ component dominated by first-order Stark. Estimate the **effective** dipole difference $\Delta\mu_{\mathrm{eff}}$ such that $h\, d\nu/dE = \Delta\mu_{\mathrm{eff}}$.

Solution.

Convert: $2.50\ \mathrm{MHz/(kV/cm)} = 2.50 \times 10^6\ \mathrm{Hz/(10^5\ V/m)} = 25\ \mathrm{Hz\,m/V}$.

$\Delta\mu_{\mathrm{eff}} = h\, d\nu/dE = 6.626 \times 10^{-34} \times 25 = 1.656 \times 10^{-32}\ \mathrm{C\,m}$.

In Debye: $1.656 \times 10^{-32}/(3.33564 \times 10^{-30}) = 4.97 \times 10^{-3}$ D.

Answer: $\boxed{\Delta\mu_{\text{eff}} \approx 5.0 \times 10^{-3} \text{ D}}$.

N7. Quadratic Stark coefficient → polarizability

A line shows $\Delta\nu = +0.90$ MHz at $E = 12.0$ kV/cm with negligible linear term. Find differential polarizability $\Delta\alpha$ from $h\Delta\nu = 1/2\,\Delta\alpha E^2$.

Solution.

$E = 12 \text{ kV/cm} = 1.2 \times 10^6 \text{ V/m}.$

$h\Delta\nu = 6.626 \times 10^{-34} \times 0.90 \times 10^6 = 5.963 \times 10^{-28}$ J.

$\Delta\alpha = 2h\Delta\nu/E^2 = 2(5.963 \times 10^{-28})/(1.44 \times 10^{12}) = 8.28 \times 10^{-40}$ C m^2/V.

Answer: $\boxed{8.3 \times 10^{-40} \text{ C m}^2/\text{V}}$.

N8. Field needed for a given Stark crossing

A fixed CO_2 laser is $\Delta\tilde{\nu} = +0.030$ cm^{-1} above the zero-field line. The measured linear Stark slope (in wavenumber) is $d\tilde{\nu}/dE = 1.20 \times 10^{-4}$ cm^{-1}/(kV/cm). Find E.

Solution.

$E = \Delta\tilde{\nu}/(d\tilde{\nu}/dE) = 0.030/(1.20 \times 10^{-4}) = 250 \text{ kV/cm}.$

Answer: $\boxed{2.5 \times 10^2 \text{ kV/cm}}$.

N9. Dipole from two M components

Two $\Delta M = 0$ components have slopes $+4.0$ and $+1.0$ MHz/(kV/cm). If their Stark shifts are $\Delta\nu = (\mu/h)\,C(J,M)\,E$ with the **same** μ but different C, find the ratio C_1/C_2.

Solution.

$C_1/C_2 = (d\nu/dE)_1/(d\nu/dE)_2 = 4.0/1.0 = 4.$

Answer: $\boxed{4:1}$.

N10. Uncertainty from field calibration

With $dv/dE = 3.00\ \mathrm{MHz/(kV/cm)}$ and electric field known to 10^{-4} relative, what is the **relative** uncertainty in inferred μ (other errors negligible)?

Solution.

$\mu \propto dv/dE$. Field scale error ϵ_E propagates 1:1 into slope and hence μ: $\delta\mu/\mu = \delta E/E = 10^{-4}$.

Answer: $\boxed{1.0 \times 10^{-4}}$.

Analytical (5)

A6. Transition Stark shift

Show $\Delta\nu(E) = [\Delta W'(E) - \Delta W''(E)]/h$. Expand to first and second order.

Solution.

Level shifts: $\Delta W = -\mu_{\|}E + 1/2\,\alpha E^2 + \cdots$.

Difference for upper/lower: $\Delta\nu = \frac{1}{h}[-\Delta\mu_{\|}E + 1/2\,\Delta\alpha E^2 + \cdots]$, with $\Delta\mu_{\|} = \mu'_{\|} - \mu''_{\|}$. ✔

A7. Matrix-element coefficient $C(J, M)$

For a linear rotor with Λ-doubling enabling first-order Stark, the linear term takes $\Delta W^{(1)} = -\mu E\, C(J, M)$. Show that C must be **odd** in M and vanishes for $M = 0$.

Solution.

The linear expectation involves orientation $\langle\cos\theta\rangle \propto M$ for $\Delta M = 0$ components; symmetry under $M \to -M$ flips sign; at $M = 0$, orientation averages to zero. Hence $C(-M) = -C(M)$, $C(0) = 0$. ✔

A8. Distinguishing linear vs quadratic regimes

Derive a log–log test: plotting $\log\Delta\nu$ vs $\log E$ gives slope 1 for linear Stark, 2 for quadratic.

Solution.

If $\Delta\nu \propto E^p$, then $\log\Delta\nu = p\log E + \text{const}$. Fit p to diagnose regime. ✔

A9. Combining multiple fixed laser lines

Explain how multiple ν_L values map out Stark curves and overdetermine μ and α.

Solution.

Each ν_L intersects $\nu_0 + \Delta\nu(E)$ at different E; collecting many (E, ν_L) pairs constrains linear and quadratic coefficients via least squares, improving precision and catching systematics (field offsets). ✔

A10. Field plates & diffraction

Why is Stark spectroscopy usually extracavity?

Solution.

To reach large E, plate spacing ~1 mm → strong diffraction/clipping inside resonator → intolerable cavity loss. Extracavity cell avoids destabilizing the laser; sensitivity recovered via modulation + lock-in. ✔

Qualitative (5)

Q6. Why Stark in the "fingerprint" region

Strong fixed lasers (CO_2, N_2O, HF/DF) populate 3–5 µm and 10 µm where many vibrational bands lie. Stark tuning lets you "scan" molecules without a tunable high-power source.

Q7. Accuracy budget

Absolute frequency accuracy (laser metrology at 20–40 kHz) + field accuracy (10^{-4}) → dipole moments with high precision; field metrology often dominates.

Q8. Modulating E

Small E-modulation yields derivative detection in E, rejecting intensity noise and slow drifts; identical in spirit to lock-in FM techniques.

Q9. Beam experiments

Stark with tunable lasers in molecular beams at sub-Doppler resolution yields excited-state dipoles with minimal collisional shifts/broadening.

Q10. FIR generation by difference frequency

Mix fixed CO_2 line with tunable CO_2 waveguide laser in a MIM diode to generate coherent FIR; then perform Stark scans over broad ranges efficiently.
