Q.5.

$\tau_{co} = 10 ms$, $\omega_R = \frac{\mu \tilde{E}_o}{\hbar}$, $\mu_{co} = 0.12$ Debye

(a) Continuous Laser Beam

Area of the laser beam $= \frac{\pi d^2}{2}$

$\therefore I = \frac{P}{A}$ & $I = \frac{1}{2} c \epsilon_o E_o^2$ (already derived)

$\Rightarrow E_o = \sqrt{\frac{2P}{c \epsilon_o A}}$

for 10 mW laser $E_o^1 = 3.1$ kV/m

for 1 W laser $E_o^2 = 31.0$ kV/m

Now

1 Debye $= 3.3356 \times 10^{-30}$ C-m

$\therefore \mu = 4.0028 \times 10^{-31}$ C-m

$\therefore$

for 10 mW laser

$$\omega_R = \frac{(4.0028 \times 10^{-31})(3.1 \times 10^3)}{1.05 \times 10^{-34}}$$

$\therefore \omega_R^1 = 1.18 \times 10^8$ rad/s

for 1 W laser

$\omega_R^2 = 1.18 \times 10^9$ rad/s

(b) Pulsed Laser Beam

Area $= \frac{\pi d^2}{2}$, $P = \frac{\text{Energy}}{\text{time}} = \frac{10 mJ}{10 ns} = 10^6$ W

$\therefore E_o = 4.9 \times 10^7$ V/m

$\therefore \omega_R = 1.88 \times 10^{11}$ rad/s

(c) Broadening

$$\Gamma = \frac{1}{\tau} = \frac{1}{10 \times 10^{-3}} = 100 \text{ Hz}$$

Now,

$$\Delta E \, \Delta t \geq \frac{\hbar}{2}$$

if $\Delta t \sim \tau$ then $\Delta E \geq \frac{\Gamma \hbar}{2}$

$$\therefore \hbar \Delta\omega \geq \frac{\Gamma\hbar}{2} \Rightarrow \Delta\omega_{natural} = \frac{\Gamma}{2}$$

$$\therefore \Delta\omega_{natural} = 50 \text{ rad/s}$$

($\because$ spontaneous emission is not an issue as it completes many Rabi Oscillations before decaying)

Q. 6.

$\Delta\nu \sim \tau^{-1}$, wavenumber $= \Delta\nu / c$ (cm^{-1})

- 10 fs pulse

$\Delta\nu = 10^{14}$ Hz $= 10^{8}$ MHz
$\Delta\bar{\lambda} = 3.33 \times 10^{3}$ cm^{-1}

- 10 ns pulse

$\Delta\nu = 100$ MHz
$\Delta\bar{\lambda} = 3.33 \times 10^{-3}$ cm^{-1}

- 10 μs pulse

$\Delta\nu = 0.1$ MHz
$\Delta\bar{\lambda} = 3.33 \times 10^{-6}$ cm^{-1}

Q.7.

Maxwell's distribution of gas molecules with velocity in $v + dv$ is

$$g(v) \propto \exp\{-\beta \times K.E.\}$$

where $KE = \frac{1}{2} m v^2$, $\beta = \frac{1}{k_B T}$

$\therefore$ Normalizing, we get

$$g(v) = \left(\frac{\beta m}{2\pi}\right)^{1/2} \exp\left\{-\beta \frac{m v^2}{2}\right\}$$

Now,

Doppler shift is given by

$$\Delta\omega = \vec{k_0} \cdot \vec{V}$$

$$\therefore \quad \omega - \omega_0 = \frac{2\pi}{\lambda_0} \hat{r} \cdot \vec{V}$$

(for simplicity assume 1D i.e. polarized light)

$$\therefore 2\pi (\nu - \nu_0) = \frac{2\pi \nu_0}{c} (V)$$

$$\Rightarrow \nu = \nu_0 \left(1 + \frac{V}{c}\right)$$

$\therefore$ The frequency distribution is now Maxwellian

$$\therefore \quad V = c\left(\frac{\nu - \nu_0}{\nu_0}\right)$$

$$\Rightarrow g(\nu) \propto \exp\left\{-\beta \frac{mc^2}{2}\left(\frac{\nu - \nu_0}{\nu_0}\right)^2\right\}$$

again, normalizing $\quad \left[A = \left(\frac{\beta mc^2}{2\nu_0^2} \times \frac{1}{\pi}\right)^{1/2}\right.$

$$\therefore g(\nu) = \frac{1}{\nu_0}\left(\frac{\beta mc^2}{2\pi}\right)^{1/2} \exp\left\{-\beta \frac{mc^2 (\nu - \nu_0)^2}{2\nu_0^2}\right\}$$

re-writing

$$g(\nu) = \frac{1}{\nu_0}\left(\frac{mc^2}{2\pi k_B T}\right)^{1/2} \exp\left\{-\frac{mc^2(\nu-\nu_0)^2}{2k_B T\,\nu_0^2}\right\}$$

a) To find the FWHM

$$g(\nu_1) = \frac{1}{2}\cdot g(\nu_0) \quad \& \quad g(\nu_2) = \frac{1}{2}\cdot g(\nu_0)$$

$$\text{FWHM} = |\nu_1 - \nu_2|$$

Let

$$g(\nu) = \frac{1}{\sqrt{2\pi}\cdot\sigma}\exp\left\{-\frac{(\nu-\nu_0)^2}{2\sigma^2}\right\}$$

where, $\sigma = \left(\frac{\nu_0^2}{\beta mc^2}\right)^{1/2}$

then,

$$g(\nu_0)\cdot\frac{1}{2} = \frac{1}{\sqrt{2\pi}\,\sigma}\exp\left\{-\frac{(\nu_1-\nu_0)^2}{2\sigma^2}\right\}$$

$$\therefore \frac{1}{\sqrt{2\pi}\cdot\sigma}\cdot\frac{1}{2} = \frac{1}{\sqrt{2\pi}\cdot\sigma}\exp\left\{-\frac{(\nu_1-\nu_0)^2}{2\sigma^2}\right\}$$

$$\Rightarrow \ln\left(\frac{1}{2}\right) = -\frac{(\nu_1-\nu_0)^2}{2\sigma^2}$$

$$\therefore (\nu_1-\nu_0)^2 = 2\sigma^2\ln(2)$$

$$\therefore \nu_1 = \nu_0 \pm \sigma\sqrt{2\ln(2)}$$

$$\therefore \Delta\nu = 2\sigma\sqrt{2\ln(2)}$$

$$\therefore \text{FWHM} = 2\nu_0\left(\frac{k_B T\sqrt{2\ln 2}}{mc^2}\right)^{1/2}$$

Clearly, $\Delta\nu \propto \sqrt{T}$

(b)

$\lambda_0 = 589.1 \text{ nm}$, $\tau = 16 \text{ ns}$, $m_{Na} = 39 \times 10^{-27} \text{ kg}$

$\therefore \nu_0 = \dfrac{3 \times 10^8}{589.1 \times 10^{-9}} \text{ Hz} = 5.093 \times 10^{14} \text{ Hz}$

$\therefore \Delta\nu = 10.186 \left(\dfrac{k_B T \sqrt{2\ln 2}}{m_{Na} \, c^2} \right)^{1/2} \times 10^{14} \text{ Hz}$

$= 2.403 \times 10^9 \text{ Hz}$ at 300 K

$= 4.387 \times 10^9 \text{ Hz}$ at 1000 K

Natural linewidth: $\dfrac{\Gamma}{2} = \dfrac{1}{2\tau}$

$\therefore \Delta\nu_{nat} = \dfrac{1}{4\pi\tau} = 4.974 \times 10^6 \text{ Hz}$

$\therefore$ Doppler broadening is 3 times more than natural brodening.

Q. 8.

Assume that the molecule interacts with the beam for a finite time (say τ)

Then the distribution is given as the Fourier Transform :

$$g(\omega) = \int_{-\tau/2}^{\tau/2} E_0 \cos(\omega_0 t) \, e^{-i\omega t} \, dt$$

$$\therefore g(\omega) = \mathrm{Re} \left\{ \frac{E_0}{2} \int_{-\tau/2}^{\tau/2} \left(e^{i\omega_0 t} + e^{-i\omega_0 t} \right) e^{-i\omega t} \, dt \right\}$$

$$= \mathrm{Re} \left\{ \frac{E_0}{2} \int_{-\tau/2}^{\tau/2} e^{-i(\omega - \omega_0) t} \, dt \right\} + F(\omega + \omega_0)$$

we consider a near resonance case so $|\omega - \omega_0| << \omega_0$

& $\omega + \omega_0 \approx 2\omega_0$

Assume $2\omega_0$ to be large enough such than many oscillations are completed in the interval 'τ'

Then we can average out the second term to

$$\therefore \quad g(\omega) = \frac{E_0}{2} \, Re \left\{ \int_{-\tau/2}^{\tau/2} e^{-i(\omega-\omega_0)t} \, dt \right\}$$

$$= \frac{E_0}{2} \frac{\sin\left[(\omega-\omega_0)\tau/2\right]}{(\omega-\omega_0)} \times 2$$

$$\therefore \quad g(\omega) = E_0 \frac{\sin\left[(\omega-\omega_0)\tau/2\right]}{(\omega-\omega_0)}$$

Q. 9.

$$\frac{I}{I_0} = \exp\left\{-\sigma(N_0 - N_1)L\right\}$$

$$\sigma = 4 \times 10^{-22} \text{ cm}^{-1}, \quad L = 1\text{m} = 100 \text{ cm}$$

to calculate $\dfrac{N_1}{N_0} = e^{-\beta(E_1 - E_0)}$

$$\Delta E = h\nu = hc\bar{\lambda} \qquad (\bar{\lambda} = 5500 \text{ cm}^{-1})$$
$$= 1.089 \times 10^{-19} \text{ J}$$

$$\therefore \quad \frac{N_1}{N_0} = 5.1 \times 10^{-12} \implies 1 - \frac{N_1}{N_0} \approx 1$$

Now, N_0 can be calculated from the molar fraction using the partial pressure

$$P_{NO} = x_{NO} P_{atm}$$

$$\therefore \quad x_{NO} = \frac{10^{-6} \times 10^{-3} \text{ Bar}}{1 \text{ Bar}}$$

$$\therefore \quad N_0 = 6.023 \times 10^{14} \quad (\text{in } 1 \text{ mol.})$$

$$\therefore \quad \frac{I}{I_0} = \exp\left\{-\sigma N_0 \left\{1 - \frac{N_1}{N_0}\right\} L\right\}$$

$$\sim \exp\left\{-10^{-10}\right\} \sim 1$$

$\therefore \quad I \approx I_0 \implies$ almost no absorption

To increase the absorption, we have to vary the parameters σ, ΔN, L

We can only change L. Thus, we have to find a way to increase L.

We can do this by constructing an Optical Parametric Amplifier type cavity which effictively increases the path length manifold.