Problem Statement: A monochromatic laser is tuned near resonance with the $R_1(13)$ transition in the (0,0) vibrational band of the $A^2\Sigma - X^2\Pi$ electronic transition of OH in a flame. The flame gases are at $T = 2000$ K and $P = 100$ kPa. The rate of collisional transfer out of the upper and lower energy levels of the transition is $10^{10}$ sec$^{-1}$, and the rate of pure dephasing collisions is $10^{10}$ sec$^{-1}$.

Find:
1. $A_{21} / \gamma_{rad,exo}$ for the $R_1(13)$ transition
2. The value of $|\omega - \omega_o|$ for which $|\chi'(\omega)|$ is a maximum. Neglect Doppler broadening.
3. The peak value of the resonance induced phase shift $|\Delta k_{res} L|$ as the laser beam passes through the cell.

$J'' = 13.5$, $J' = 14.5$, $v'' = 0$, $v' = 0$, $\frac{\omega_e}{2\pi c} = 32,603.003$ cm$^{-1}$, $A_{21} = 2.691 \times 10^5$ sec$^{-1}$,

$Q_{\text{trans1}} = Q_{\text{trans2}} = \gamma_1 = \gamma_2 = 10^{10}$ sec$^{-1}$, $Q_{\text{deph}} = \frac{1}{T_2} = 10^{10}$ sec$^{-1}$

For OH:

$B_0 = 18.51$ cm$^{-1}$, $\omega_c = 3735$ cm$^{-1}$, $g_{0,\text{elec}} = 4$
Solution:

(1) \[ \gamma_{rad,ceo} = \frac{e^2 \omega_a^2}{6 \pi \varepsilon_0 m_e c^3} \]

\begin{align*}
\gamma_{rad,ceo} &= \frac{(1.602 \times 10^{-19} \ C)^2}{6 \pi \left( \frac{8.854 \times 10^{-12} \ C^2}{J \ m} \right)} \left( \frac{9.109 \times 10^{-31} \ kg}{2.998 \times 10^8 \ m/s} \right)^2 \\
&= 2.383 \times 10^8 \frac{C^2 \ s^{-2}}{kg \ m^3 \ s^{-3}} = 2.383 \times 10^8 \ s^{-1}
\end{align*}

Answer: \[ \frac{A_{a1}}{\gamma_{rad,ceo}} = \frac{\gamma_{rad,actual}}{\gamma_{rad,ceo}} = \frac{2.691 \times 10^5}{2.383 \times 10^8} = 0.00114 \]

(2) The real part of the susceptibility peaks at

\[ \frac{\omega - \omega_d}{\Delta \omega_d} = \pm 0.5 \ , \quad \Delta \omega_d = \text{FWHM} \]

\[ \Delta \omega_d = \gamma_{rad} + Q_{\text{trans1}} + Q_{\text{trans2}} + 2 Q_{\text{deph}} = 4 \times 10^{10} \ \text{sec}^{-1} \]

\[ |\omega - \omega_d| = 0.5 \times 4 \times 10^{10} = 2 \times 10^{10} \ \text{sec}^{-1} \ at \ peak \ of \ \chi' \]

Answer: \[ \frac{|\omega - \omega_d|}{2 \pi c} = 0.106 \ \text{cm}^{-1} \ at \ peak \ of \ \chi' \]

(3) We need to find \( \chi''_0 \) for the R1(13) transition:

\[ \chi''_0 = \frac{1}{4 \pi^2} \left( \frac{g_2}{g_1} \right) \left( n_1 - n_2 \right)^3 \frac{A_{a1}^3 \gamma_{rad}}{\Delta \omega_d} \]
\[ \lambda_{21} = \frac{c}{\nu_{21}} = \frac{1}{\nu_{21}} \]

\[ = \frac{2\pi c}{\omega_a} = 306.7 \text{ nm} = 3.067 \times 10^{-7} \text{ m} \]

Find the number density of OH:

\[ P\forall = N_{\text{tot}} k_B T \quad \Rightarrow \quad n_{\text{tot}} = \frac{N_{\text{tot}}}{\forall} = \frac{P}{k_B T} = \frac{100 \times 10^3 \text{ } J / m^3}{(1.38 \times 10^{-23} \text{ } J / K)(2000 \text{ } K)} = 3.62 \times 10^{24} \text{ } m^{-3} \]

\[ n_{\text{OH}} = 0.01 n_{\text{tot}} = 3.62 \times 10^{22} \text{ } m^{-3} \]

Find the number density of OH molecules in the \( J'' = 13.5, v'' = 0 \) level (level 1):

\[ \frac{n_1}{n_{\text{OH}}} = g_1 \exp \left[ -\frac{\varepsilon_1}{h c}\left(\frac{h c}{k T}\right) \right] \]

For the \( R_1(13) \) transition:

\[ J'' = 13.5, J' = 14.5, v'' = 0, v' = 0, \quad \frac{\omega_a}{2\pi c} = 32,603.003 \text{ cm}^{-1}, \quad A_{21} = 2.691 \times 10^5 \text{ sec}^{-1}, \]

\[ Q_{\text{trans1}} = Q_{\text{trans2}} = \gamma_1 = \gamma_2 = 10^{10} \text{ sec}^{-1}, \quad Q_{\text{deph}} = \frac{1}{T_2} = 10^{10} \text{ sec}^{-1} \]

For OH:

\[ B_0 = 18.51 \text{ cm}^{-1}, \quad \omega_e = 3735 \text{ cm}^{-1}, \quad g_{0,\text{elec}} = 4 \]

For level 1,

\[ g_1 = 2J'' + 1 = 28, \quad \frac{\varepsilon_1}{h c} = F(J'') + G(v'') = B_0 J'' (J'' + 1) + \omega_v \left( v'' + \frac{1}{2} \right) = 5491 \text{ cm}^{-1} \]

The partition functions for OH are given by:

\[ Z_{\text{elec}} = g_{0,\text{elec}} = 4, \quad Z_{\text{vib}} = \frac{\exp(-\theta_{\text{vib}}/2T)}{1 - \exp(-\theta_{\text{vib}}/T)} = 0.280 \quad \theta_{\text{vib}} = \frac{h c \omega_v}{k_B} \]
\[ Z_{\text{rad}} = \frac{kT}{hcB_0} = 75.1 \quad \frac{hc}{k_B} = 1.439 \ K/cm^{-1} \]

\[ \frac{n_1}{n_{\text{OH}}} = \frac{28 \exp\left[-\left(\frac{5491 \ cm^{-1}}{(1.439 \ K/cm^{-1})(2000 \ K)}\right)\right]}{(4)(0.280)(75.1)} = 0.0064 \]

\[ n_1 = 0.0064 \ n_{\text{OH}} = 2.3 \times 10^{20} \ m^{-3} \]

Now find \( \chi'' \) and the maximum phase shift:

\[ \chi'' = \frac{1}{4\pi^2} \left\{ \frac{g_2 n_1 - g_1 n_2}{g_1} \right\} \tilde{\lambda}^3 \chi_{\text{rad}} \]

\[ = \frac{1}{4\pi^2} \left\{ \frac{30}{28} \left(2.3 \times 10^{20} - 0 \ m^{-3}\right) \left(3.067 \times 10^{-7} \ m^{-3}\right)^3 \left(2.691 \times 10^5 \ sec^{-1}\right) \right\} \]

\[ = 1.2 \times 10^{-6} \]

The real part of the susceptibility, which gives rise to the phase shift, peaks at \( \omega - \omega_a = -\Delta \omega_a / 2 \)

\[ \chi' = -\chi'' \frac{\Delta x}{1 + (\Delta x)^2} \quad \Delta x = \frac{2(\omega - \omega_a)}{\Delta \omega_a} = -1 \text{ at peak of real part of } \chi \]

\[ \chi' = -\chi'' \frac{-1}{1 + (-1)^2} = \frac{\chi''}{2} = 6.0 \times 10^{-7} \text{ at peak of real part of } \chi \]

\[ \Delta k_{\text{res}} = \left(\frac{\pi}{\lambda}\right) \chi' = \frac{\pi(6.0 \times 10^{-7})}{3.067 \times 10^{-7} / m} = 6.1 \ m^{-1} \]

Answer:

\[ \Delta k_{\text{res}}L = (6.1 \ m^{-1})(0.1 \ m) = 0.61 \ radians \]

\[ \approx 0.097 \text{ cycles of light, phase change of } 35^\circ \]