Chemistry 620
Analytical Spectroscopy
PROBLEM SET 2: Due 02/28/08

1. The dielectric constant of water (not ice or steam) varies from 88.00 at 0°C to 55.33 at 100°C. Explain this behavior. Over the same range in temperature, the index of refraction (λ = 589.3 nm) goes from roughly 1.33 to 1.32. Why is the change in *n* so much smaller than the corresponding change in ε?

   The dielectric constant is lower at high temperature because the permittivity, i.e., capacity of water to stabilize charge by dipole rearrangement, is undermined by thermal motion at high temperature. The refractive index (n=c/v) is more a measure of electronic polarization, i.e. how tightly the electrons are bound, and, their impact on the velocity of EMR traversing the medium. This observation illustrates the fact that there are limits on relations such as $n^2=\varepsilon/\varepsilon_0$.

2. Consider a linearly polarized plane electromagnetic wave traveling in the +x direction in a dielectric that has refractive index equal to 1.77 and the xy plane as its plane of vibration. Given that its frequency is 614.3 THz and its amplitude is E_0 = 0.25 V/m,
   a. find the period and wavelength of the wave,
      $$\lambda = v/\nu = (c/n)/\nu = (0.56 \cdot 2.998e8\, m/s)/614.3e12\, Hz = 273.3e-9\, nm$$
      $$T = 1/\nu = 1/614.3e12\, Hz = 1.628\, fs$$
   b. write an expression for E(t),
      $$E = E_0 \cos\left(\omega\left(t - \frac{1}{v}z\right) + \phi_0\right) = 0.25\tfrac{V}{m}\cos\left(1.229\pi \times 10^{15} s^{-1}\left(t - \frac{z}{0.56c}\right)\right)$$
      $$= 0.25\tfrac{V}{m}\cos\left(3.86 \times 10^{15} s^{-1} t - 2.277 \times 10^{7} z\right)$$
   c. find the irradiance of the wave falling on a detector (outside the dielectric)
      $$\mathcal{E} = \frac{c\varepsilon_0}{2}E_0^2 = \frac{3e8\,\frac{m}{s} \cdot 8.854e-12\,\frac{C^2}{Nm^2}}{2} 0.0625\frac{V^2}{m^2} = 8.3e-5\frac{W}{m^2}$$

3. A plane, harmonic, linearly polarized light wave traveling in a piece of glass has an electric field intensity given by
   $$E_z = E_0 \cos\left(\pi 10^{15}\left(t - \frac{z}{0.59c}\right)\right)$$
   Calculate
   a) the wavelength of the light in the glass,
      $$\lambda = v/\nu = 0.59 \cdot 3e8\,\tfrac{m}{s} / 5e14\,\tfrac{1}{s} = 354 nm;$$
   b) the index of refraction of the glass,
      $$n = c/v = c/0.59c = 1.69$$

c) the phase shift between the wave entering and exiting the glass if the glass is 1 mm thick.

The phase difference arises from the difference in the speed (or wavelength) of the light inside the glass -

$$\Delta\phi = \Delta kz = \left(\frac{\omega}{v} - \frac{\omega}{c}\right)d = \left(\frac{\omega}{c/n} - \frac{\omega}{c}\right)d = \frac{\omega}{c}(n-1)d$$

$$= \frac{2\pi \times 5e14\,\frac{1}{s}}{3e8\,\frac{m}{s}}(1.695-1)0.001m = 7278.02\,rad \Rightarrow 2.09\,rad$$

Alternatively, $\lambda_0 = c/\nu = 3e8\,\frac{m}{s}/5e14\,\frac{1}{s} = 600\,nm$

$$\Delta\phi = \Delta kz = \left(\frac{2\pi}{\lambda} - \frac{2\pi}{\lambda_0}\right)d = \left(\frac{n2\pi}{\lambda_0} - \frac{2\pi}{\lambda_0}\right)d = \frac{2\pi}{\lambda_0}(n-1)d$$

$$= 1.047e7m^{-1}(1.695-1)0.001m = 7278.02\,rad \Rightarrow 2.09\,rad$$

4. Show that for an ideal substance that has a single resonant frequency ω_0, the index of refraction is approximated by

$$n \approx 1 + \frac{Ne^2}{2m_e\varepsilon_0(\omega_0^2 - \omega^2)}$$

$$n^2 = 1 + \chi = 1 + \frac{Ne^2}{m\varepsilon_0}\frac{1}{\left(\omega_0^2 - \omega^2\right) + 2i\gamma\omega}$$

$$\frac{Ne^2/m\varepsilon_0}{\left(\omega_0^2 - \omega^2\right) + 2i\gamma\omega} = \frac{Ne^2/m\varepsilon_0}{\left(\omega_0^2 - \omega^2\right) + 2i\gamma\omega}\frac{\left(\omega_0^2 - \omega^2\right) - 2i\gamma\omega}{\left(\omega_0^2 - \omega^2\right) - 2i\gamma\omega} = \frac{Ne^2/m\varepsilon_0\left(\omega_0^2 - \omega^2\right) - 2i\gamma\omega}{\left(\omega_0^2 - \omega^2\right)^2 - 4\gamma^2\omega^2}$$

In gases, atoms or molecules do not interact. Collisions are essentially elastic, so the damping coefficient is negligible. The expresssion for n^2 becomes

$$n^2 = 1 + \frac{Ne^2}{m\varepsilon_0}\frac{1}{\left(\omega_0^2 - \omega^2\right)}$$

Remembering that if $n^2 \equiv (1+x)^2 \equiv 1 + 2x + x^2$

then for small x, $n^2 \approx 1 + 2x$. This implies that

$$n \approx 1 + \frac{Ne^2}{2m\varepsilon_0}\frac{1}{\left(\omega_0^2 - \omega^2\right)} \approx (1+x)$$

Similar logic uses a binomial series to compute of square roots close to 1:

$$(1+x)^{\frac{1}{2}} = 1 + \frac{1}{2}x - \frac{1}{4\cdot 2!}x^2 + \frac{3}{8\cdot 3!}x^3 + \ldots$$

$$n = \left(1 + \frac{Ne^2}{m\varepsilon_0}\frac{1}{\left(\omega_0^2 - \omega^2\right)}\right)^{\frac{1}{2}} \approx 1 + \frac{Ne^2}{2m\varepsilon_0}\frac{1}{\left(\omega_0^2 - \omega^2\right)}$$

5. At 500 nm, germanium has a refractive index of 3.47-1.4i. Calculate the absorption coefficient of germanium at this wavelength.

$$\Phi = \Phi_0 e^{-2\frac{n_{imag}\omega}{c}z} = \Phi_0 e^{-kb}$$

$$kb = 2\frac{n_{imag}\omega}{c}z$$

$$\omega = 2\pi\nu = 2\pi c/\lambda = 2\pi \cdot 3e8ms^{-1}/5.0e-7m = 3.77e15s^{-1}$$

$$k = 2\frac{n_{imag}\omega}{c} = 2\frac{1.4 \cdot 3.77e15s^{-1}}{3e8ms^{-1}} \times \frac{1m}{100cm} = 3.52e5cm^{-1}$$

6. Calculate the electric field and irradiance necessary for the polarization due to second-order effects to be a third as large as the polarization due to first-order effects. Assume the second-order electric susceptibility for the material irradiated is 0.005 times the first-order susceptibility.

$$P = P_1 + P_2 + ... = \chi_1 E + \chi_2 E^2 + ...$$

$$Goal: \quad 0.3\overline{3}P_1 = P_2 \; if \; \chi_2 = 0.005\chi_1$$

$$0.3\overline{3}\chi_1 E_0 = \chi_2 E_0^2 = 0.005\chi_1 E_0^2$$

$$0.3\overline{3} = 0.005 E_0$$

$$E_0 = \frac{0.3\overline{3}}{0.005} = 6\overline{6}\frac{V}{m}$$

$$\mathcal{E} = \frac{c\varepsilon_0}{2}E_0^2 = \frac{3e8\frac{m}{s} \cdot 8.854e-12\frac{C^2}{N \cdot m^2}}{2} 4..44e3\frac{V^2}{m^2}$$

$$= 5.90\frac{C^2V^2}{Nm^3s} = 5.90\frac{W}{m^2}$$

7. One of the ways investigators extend the spectral range of Ti:sapphire lasers deeper into the IR is to mix the output with that of a monochromatic laser. Select a laser for this purpose and estimate the range of IR wavelengths that would be available by mixing the Ti:sapphire fundamental (λ~ 650 - 1100 nm) with it.

$$\lambda_{\min}^{Ti:Sa} = 0.65\ \mu m$$

$$\lambda_{\max}^{Ti:Sa} = 1100\ nm$$

$$\nu_{mono} = c/\lambda_{mono} = \frac{3e8}{1064e-9} = 2.82e14$$

$$\nu_{\min}^{tune} = \frac{3e8}{1100e-9m} = 2.73e14; \nu_{\max}^{tune} = \frac{3e8}{650e-9} = 4.61e14$$

$$\nu_{\max}^{mix} = \nu_{\max}^{tune} - \nu_{mono} = 1.47e14s^{-1} \Rightarrow 2.04\ \mu m$$

$$\nu_{\min}^{mix} = \nu_{mono} - \nu_{\min}^{tune} = 0.09e14s^{-1} \Rightarrow 33.3\ \mu m$$

8. Ordinarily, the efficiency of SHG is very low. However, when special efforts are made to achieve phase matching, the SHG production is so efficient that the depletion of the pump beam must be considered. In this case the SHG production is given by

$$\mathcal{E}_{SHG} = 2\frac{\omega^2 d^2 l^2}{n_1^2 n_2 c^3 \varepsilon_0}(1)^2 \mathcal{E}_{fund}^2$$

Calculate the efficiency of SHG for a 10 W pulsed Nd:YAG laser beam focused down to 800 μm^2 on a KD_2PO_4 surface if n_1 and n_2 are 1.495 and 1.515, respectively, l is the coherence length and the pulse duration is 1 ps and rep rate is 1 MHz. The effective non-linear optical coefficient of KD_2PO_4 is a single element tensor, d_{eff} = 5.25e-24 mV^{-1}.

$$l_c = \left|\frac{\lambda}{4(n_1 - n_2)}\right| = \left|\frac{1064nm}{4(1.495 - 1.515)}\right| = 1.330e-5m$$

$$\mathcal{E}_{fund} = \frac{\bar{\Phi}/(t_{pulse}f_{rep})}{\text{A}} = \frac{10.0W\ /\ 1ps \cdot 1MHz}{2000\mu m^2} = \frac{10.0M\,W}{2e-9m^2} = 5e15\frac{W}{m^2}$$

$$\omega = 2\pi\frac{c}{\lambda} = \frac{2\pi \cdot 3e8\,\frac{m}{s}}{1064e-9m} = 1.7698e15\frac{1}{s}$$

$$e_{SHG} = \frac{\mathcal{E}_{SHG}}{\mathcal{E}_{fund}} = 2\frac{\omega^2 d^2 l^2}{n_1^2 n_2 c^3 \varepsilon_0}(1)^2 \mathcal{E}_{fund}$$

$$= 2 \cdot \frac{3.132e30\frac{1}{s^2}\left(5.25e-12\frac{m}{V}\right)^2 (1.330e-5m)^2}{2.235 \cdot 1.515 \cdot 27e24\frac{m^3}{s^3} \cdot 8.854e-12\frac{C^2}{Nm^2}} 5e15\frac{W}{m^2}$$

$$= 2 \cdot \left(2.55e7\frac{m^2}{\frac{N^2m^2}{C^2}s^2}\right)\left(\frac{(1.330e-5m)^2}{27e24\frac{m^3}{s^3} \cdot 8.854e-12\frac{C^2}{Nm^2}}\right)5e15\frac{Nm}{m^2 s}$$

$$= 2 \cdot (2.55e7)(7.3995e-25)5e15 = 0.1887$$