Advanced Physical Chemistry II
HW

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15 Lasers, Laser Spectroscopy and Photochemistry

6,12,16,19,24,33,38

15-6 Eq. 15.15 reads

$$\frac{\mathrm{d}N_2(t)}{\mathrm{d}t} = B\rho_\nu(\nu_{12})[N_1(t) - N_2(t)] - AN_2(t) \tag{15.1}$$

thus

$$\mathrm{d}t = \frac{\mathrm{d}N_2}{B\rho_\nu(\nu_{12})[N_{\text{total}} - 2N_2] - AN_2} = \frac{\mathrm{d}N_2}{B\rho_\nu(\nu_{12})N_{\text{total}} - [A + 2B\rho_\nu(\nu_{12})]N_2} \tag{15.2}$$

$$\mathrm{d}t = -\frac{1}{A + 2B\rho_\nu(\nu_{12})}\mathrm{d}\ln\{B\rho_\nu(\nu_{12})N_{\text{total}} - [A + 2B\rho_\nu(\nu_{12})]N_2\} \tag{15.3}$$

Assume $N_2(0) = 0$, we have

$$t - 0 = -\frac{\ln\{B\rho_\nu(\nu_{12})N_{\text{total}} - [A + 2B\rho_\nu(\nu_{12})]N_2\} - \ln B\rho_\nu(\nu_{12})N_{\text{total}}}{A + 2B\rho_\nu(\nu_{12})} \tag{15.4}$$

$$\mathrm{e}^{-t[A+2B\rho_\nu(\nu_{12})]} = \frac{B\rho_\nu(\nu_{12})N_{\text{total}} - [A + 2B\rho_\nu(\nu_{12})]N_2}{B\rho_\nu(\nu_{12})N_{\text{total}}} \tag{15.5}$$

$$N_2 = \frac{B\rho_\nu(\nu_{12})N_{\text{total}}}{A + 2B\rho_\nu(\nu_{12})}\left\{1 - \mathrm{e}^{-t[A+2B\rho_\nu(\nu_{12})]}\right\} \tag{15.6}$$

15-12 After the light is turned off

$$\frac{\mathrm{d}N_3}{\mathrm{d}t} = -A_{32}N_3 - A_{31}N_3 \tag{15.7}$$

suppose $t = 0, N_3 = N_3^0$ when the light is turned off

$$N_3 = N_3^0\,\mathrm{e}^{-(A_{31}+A_{32})t} \tag{15.8}$$

the observed radiative lifetime will be

$$\tau = \frac{1}{A_{31} + A_{32}} \tag{15.9}$$

15-16

$$\lambda = \frac{1}{\tilde{\nu}} = \frac{1}{(166658.484 - 163710.581)\mathrm{cm}^{-1}} = 3392.242\,\mathrm{nm} \tag{15.10}$$

which is calculated in the vacuum. To compare with experimental data in the air, we need to make a correction

$$\lambda_{\text{air}} = \frac{\lambda}{1.00029} = 3391.3\,\mathrm{nm} \tag{15.11}$$

15-19 the radiant power of each pulse

$$P_{\text{pulse}} = \frac{1.4\,\text{W}}{100\,\text{MHz} \cdot 25\,\text{fs}} = 560\,\text{kW} \tag{15.12}$$

number of photons in 1 second

$$N = \frac{1.4\,\text{J}}{hc/780\,\text{nm}} = 5.50 \times 10^{18} \tag{15.13}$$

15-24

$$N = \frac{(5.00\,\text{kW}/10\,\text{Hz}) \times 27\%}{hc/9.6\,\mu\text{m}} = 6.52 \times 10^{21} \tag{15.14}$$

15-33

$$v = \frac{400\,\text{pm} - 275\,\text{pm}}{205\,\text{fs}} = 610\,\text{m} \cdot \text{s}^{-1} \tag{15.15}$$

15-38 A is unitless, and ε has a unit $\text{m}^2 \cdot \text{mol}^{-1}$.
If the intensity of the transmitted light is 25.0%,

$$A = \lg \frac{1}{0.25} = 0.602 \tag{15.16}$$

For benzene described above

$$\varepsilon = \frac{A}{cl} = \frac{1.08}{1.42 \times 10^{-3}\,\text{mol} \cdot \text{L}^{-1} \cdot 1.21 \times 10^{-3}\,\text{m}} = 629\,\text{m}^2 \cdot \text{mol}^{-1} \tag{15.17}$$

the percentage of transmitted light is

$$\frac{I}{I_0} = \frac{1}{10^A} \times 100\% = 8.3\% \tag{15.18}$$