Experimental methods in trace gas research

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Please use the provided paper sheets to write down the solutions of the problems. Write your name and student ID number on a first page and enumerate all subsequent pages. Do not forget to hand in your paperwork after the examination.

Problem 1.

In first approximation, acetylene C_2H_2 can be considered as a molecule of linear structure with a rotational constant $B = 1.17\ cm^{-1}$.

a) How many vibrational degrees of freedom does this molecule have?

b) What rotational level of C_2H_2 does have the larger population at room temperature: the level with the rotational number $J = 5$ or that with $J = 20$?

c) A researcher is going to measure the ratio between concentrations of isotopic molecules C_2H_2 and C_2HD. He estimated the distance between the spectral lines of these species at wavenumber around 3400 cm^{-1} to be of order 0.2 cm^{-1}. Can these lines be distinguished at room temperature? Molecular weights of C_2H_2 and C_2HD are 26 and 27 g/mole, respectively.

Problem 2.

Concentrations of OH molecules in air are measured by using the tunable diode laser absorption (TDLA) method. Measurements are performed at room temperature ($T = 300\ K$) and atmospheric pressure ($P = 1.01325 \cdot 10^6\ erg/cm^2$) in vicinity of the P(5.5) spectral line with the wavenumber $\tilde{\nu} = 3367.038\ \mathrm{cm}^{-1}$ and intensity $S = 2.622 \cdot 10^{-20} \frac{cm^{-1}}{molecule \cdot cm^{-2}}$.

a) The wavenumber of the P(6.5) line is 3324.577 cm^{-1}. Find the rotational constant of the OH molecule.
b) What ratio between initial and transmitted signal is expected in cell of length $L = 1$ with 100 ppm OH in air when the laser is tuned to the center of the P(5.5) line? The spectral line profile can be considered to be Lorentzian with the width $\Delta\tilde{\nu} = 0.06\ cm^{-1}$.
c) Does the width of the spectral line profile decrease or increase if the temperature increases?

Problem 3.

A researcher is going to build an optical setup for measuring sizes and concentrations of non-absorbing spherical particles. It is expected that the particles are monodisperse with diameters smaller than 50 nm.

a) The researcher has two lasers for using in his setup with wavelengths 0.75 µm and 0.5 µm and powers 5W and 100 mW, respectively. What laser will provide a larger scattered signal?
b) The researcher decided to determine the particle number density by measuring the extinction coefficient. Sketch the experimental setup for the extinction measurements and explain how to derive the number density from the extinction measurements if the particle diameter d_p and refraction index m of the particle's substance are known.
c) The number density of particles is 10^{14} m^{-3}. What is the diameter of the particle if the volume fraction of the particles is 1 ppb?

Problem 4.

a) Which "masses", i.e. ion beam signals at a certain m/e number, can we expect to find in a mass spectrum of pure CO_2 and what ions are they derived from?
b) Measuring CO_2, cryogenically extracted from air, which isotopomers are collected at m/e=46?
c) Why is it physically possible to separate HD from ^3He by magnetic mass spectrometry, as both have the same mass of 3 atomic mass units?

Physical constants and conversion factors

Velocity of light in vacuum	c	$2.99792458 \cdot 10^{10}$ cm/s
Planck's constant	h	$6.626076 \cdot 10^{-27}$ erg/s
Electronic charge	e	$4.803206 \cdot 10^{-10}$ abs.e.s.u.
Electronic mass	m_e	$9.109390 \cdot 10^{-28}$ g
Mass of proton	m_p	$1.672623 \cdot 10^{-24}$ g
1/12 mass of the C^{12} atom	M_1	$1.660540 \cdot 10^{-24}$ g
Number of atoms in mole	N_A	$6.022137 \cdot 10^{23}$
Boltzamann's constant	k	$1.38066 \cdot 10^{-16}$ erg/K
Gas constant per mole	R	$8.31451 \cdot 10^{7}$ erg/K·mole

Conversion factors for energy units

	1 J	**1 erg**	**1 eV**	**1 K**	**1 cm^{-1}**
1 J	1	10^{7}	$6.2415 \cdot 10^{18}$	$7.2429 \cdot 10^{22}$	$5.0341 \cdot 10^{22}$
1 erg	10^{-7}	1	$6.2415 \cdot 10^{11}$	$7.2429 \cdot 10^{15}$	$5.0341 \cdot 10^{15}$
1 eV	$1.6022 \cdot 10^{-19}$	$1.6022 \cdot 10^{-12}$	1	11604	8065.5
1 K	$1.3807 \cdot 10^{-23}$	$1.3807 \cdot 10^{-16}$	$8.6174 \cdot 10^{-5}$	1	0.69504
1 cm^{-1}	$1.9864 \cdot 10^{-23}$	$1.9864 \cdot 10^{-16}$	$1.2398 \cdot 10^{-4}$	1.4388	1

Standard Atomic Weights.

Period \ Group	I	II	III	IV	V	VI	VII	VIII		
1	1520 $_{1}$H 1.0079 Hydrogen	0.008 4.003 $_{2}$He Helium								
2	20 Li 6.941 Lithium	2.6 $_{4}$Be 9.012 Berillium	10 10.81 $_{5}$B Boron	480 12.011 $_{6}$C Carbon	25 14.007 $_{7}$N Nitrogen	474000 15.999 $_{8}$O Oxygen	950 18.998 $_{9}$F Fluorine	$7\cdot10^{-5}$ 20.180 $_{10}$Ne Neon		
3	23000 $_{11}$Na 22.990 Sodium	23000 $_{12}$Mg 24.305 Magnesium	82000 26.982 $_{13}$Al Aluminium	277000 28.086 $_{14}$Si Silicon	1000 30.974 $_{15}$P Phosphorus	260 32.065 $_{16}$S Sulfur	130 35.453 $_{17}$Cl Chlorine	1.2 39.948 $_{18}$Ar Argon		
4	21000 $_{19}$K 39.098 Potassium	41000 $_{20}$Ca 40.08 Calsium	16 $_{21}$Sc 44.956 Scandium	5600 $_{22}$Ti 47.867 Titanium	160 $_{23}$V 50.942 Vanadium	100 $_{24}$Cr 51.996 Chromium	950 $_{25}$Mn 54.938 Manganese	41000 $_{26}$Fe 55.845 Iron	20 $_{27}$Co 58.933 Cobalt	80 $_{28}$Ni 58.69 Nickel
	50 63.546 $_{29}$Cu Copper	75 65.409 $_{30}$Zn Zinc	18 69.723 $_{31}$Ga Gallium	1.8 72.64 $_{32}$Ge Germanium	1.5 74.922 $_{33}$As Arsenic	0.05 78.96 $_{34}$Se Selenium	0.37 79.904 $_{35}$Br Bromine	$1\cdot10^{-5}$ 83.798 $_{36}$Kr Krypton		
5	90 $_{37}$Rb 85.468 Rubidium	370 $_{38}$Sr 87.62 Strontium	30 $_{39}$Y 88.906 Yttrium	190 $_{40}$Zr 91.224 Zirconium	20 $_{41}$Nb 92.906 Niobium	1.5 $_{42}$Mo 95.94 Molibdenum	$7\cdot10^{-4}$ $_{43}$Tc [97.907] Technetium	0.001 $_{44}$Ru 101.07 Ruthenium	$2\cdot10^{-4}$ $_{45}$Rh 102.91 Rhodium	$6\cdot10^{-4}$ $_{46}$Pd 106.42 Palladium
	0.07 107.87 $_{47}$Ag Silver	0.11 112.41 $_{48}$Cd Cadmium	0.049 114.82 $_{49}$In Indium	2.2 118.70 $_{50}$Sn Tin	0.2 121.76 $_{51}$Sb Antimony	0.005 127.60 $_{52}$Te Tellurium	0.14 126.90 $_{53}$I Iodine	$2\cdot10^{-6}$ 131.29 $_{54}$Xe Xenon		
6	3.0 $_{55}$Cs 132.90 Cesium	500 $_{56}$Ba 137.33 Barium	32 $_{57}$La 138.90 Lanthanum	3.3 $_{72}$Hf 178.49 Hafnium	2.0 $_{73}$Ta 180.95 Tantalum	1.0 $_{74}$W 183.84 Tungsten	$4\cdot10^{-4}$ $_{75}$Re 186.21 Rhenium	$1\cdot10^{-4}$ $_{76}$Os 190.23 Osmium	$3\cdot10^{-6}$ $_{77}$Ir 192.22 Iridium	0.001 $_{78}$Pt 195.08 Platinum
	0.0011 196.97 $_{79}$Au Gold	0.05 200.59 $_{80}$Hg Mercury	0.6 204.38 $_{81}$Tl Thallium	1.4 207.2 $_{82}$Pb Lead	0.048 208.98 $_{83}$Bi Bismuth	[208.98] $_{84}$Po Polonium	[209.99] $_{85}$At Astatine	[222.02] $_{86}$Rn Radon		
7	$_{87}$Fr [223.02] Francium	$6\cdot10^{-7}$ $_{88}$Ra [226.02] Radium	$_{89}$Ac [227.03] Actinium							

Abundance in Earth crust, 10^{-4} %
Symbol — Atomic number — Element — Atomic weight

1.5 $_{42}$Mo 95.94 Molibdenum

Lantanides

68 $_{58}$Ce 140.12 Cerium	9.5 $_{59}$Pr 140.91 Praseodymium	38 $_{60}$Nd 144.24 Neodymium	$_{61}$Pm [144.91] Promethium	7.9 $_{62}$Sm 150.36 Samarium	2.1 $_{63}$Eu 151.96 Europium	7.8 $_{64}$Gd 157.25 Gadolinium
1.1 $_{65}$Tb 158.92 Terbium	6.0 $_{66}$Dy 162.50 Dysprosium	1.4 $_{67}$Ho 164.93 Holmium	3.8 $_{68}$Er 167.26 Erbium	0.48 $_{69}$Tm 168.93 Thulium	5.3 $_{70}$Yb 173.04 Ytterbium	0.51 $_{71}$Lu 174.97 Lutetium

Actinides

12 $_{90}$Th 232.04 Thorium	$_{91}$Pa 231.04 Protactinium	2.4 $_{92}$U 238.03 Uranium	$_{93}$Np 237.05 Neptunium	$_{94}$Pu [244.06] Plutonium	$_{95}$Am [243.06] Americium		
$_{96}$Cm [247.06] Curium	$_{97}$Bk [247.07] Berkelium	$_{98}$Cf [251.08] Californium	$_{99}$Es [252.08] Einsteinium	$_{100}$Fm [257.10] Fermium	$_{101}$Md [258.10] Mendelevium		
$_{102}$No [259.10] Nobelium	$_{103}$Lr [262.11] Lawrencium	$_{104}$Rf [261.11] Rutherfordium	$_{105}$Db [262.11] Dubnium	$_{106}$Sg [266.12] Seaborgium	$_{107}$Bh [264.12] Bohrium	$_{108}$Hs [267] Hassium	$_{109}$Mt [268.14] Meitnerium

Formulas

$$\widehat{H}_t\Psi(\overrightarrow{R_1},\dots\overrightarrow{R_N},\overrightarrow{r_1},\dots,\overrightarrow{r_n}) = E\Psi(\overrightarrow{R_1},\dots\overrightarrow{R_N},\overrightarrow{r_1},\dots,\overrightarrow{r_n}) \quad (2.1)$$

$$\widehat{H}_t = -\frac{\hbar^2}{2}\sum_i^N\frac{\Delta_i}{M_i} - \frac{\hbar^2}{2}\sum_j^n\frac{\Delta_j}{m_e} + \sum_{i,j}\frac{Z_iZ_Je^2}{|\overrightarrow{R_i}-\overrightarrow{R_j}|} + \sum_{i,j}\frac{e^2}{|\overrightarrow{r_i}-\overrightarrow{r_j}|} - \sum_{i,j}\frac{Z_ie^2}{|\overrightarrow{R_i}-\overrightarrow{r_j}|} \quad (2.2)$$

$$\widehat{H}_e = -\frac{\hbar^2}{2}\sum_j^n\frac{\Delta_j}{m_e} + \sum_{i,j}\frac{e^2}{|\overrightarrow{r_i}-\overrightarrow{r_j}|} - \sum_{i,j}\frac{Z_ie^2}{|\overrightarrow{R_i}-\overrightarrow{r_j}|} + \sum_{i,j}\frac{Z_iZ_Je^2}{|\overrightarrow{R_i}-\overrightarrow{R_j}|}$$
$$\widehat{H}_N = -\frac{\hbar^2}{2}\sum_i^N\frac{\Delta_i}{M_i} \quad (2.3)$$

$$\widehat{H}_e\Psi_e(\vec{R}_1,\dots\vec{R}_N,\vec{r}_1,\dots,\vec{r}_n) = E_e(\vec{R}_1,\dots,\vec{R}_N)\Psi_e(\vec{R}_1,\dots\vec{R}_N,\vec{r}_1,\dots,\vec{r}_n) \quad (2.4)$$

$$\Psi(\vec{R}_1,\dots\vec{R}_N,\vec{r}_1,\dots,\vec{r}_n) = \sum_k\Phi_n(\vec{R}_1,\dots,\vec{R}_N)\Psi_e^k(\vec{R}_1,\dots\vec{R}_N,\vec{r}_1,\dots,\vec{r}_n) \quad (2.5)$$

$$\left(-\frac{\hbar^2}{2}\sum_i^N\frac{\Delta_i}{M_i} + E_e(R_1,\dots,R_N)\right)\Phi_k(\vec{R}_1,\dots,\vec{R}_N) = E\Phi_k(\vec{R}_1,\dots,\vec{R}_N) \quad (2.6)$$

$$E_e(R) = 4\epsilon\left(\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^6\right) = \epsilon\left(\left(\frac{R_m}{R}\right)^{12} - 2\left(\frac{R_m}{R}\right)^6\right) \quad (2.7)$$

$$\widehat{H}_{rot}\Phi_r(q_r) = E_{rot}\Phi_r(q_r)$$
$$\widehat{H}_1\Phi_v(q_v) = E_1\Phi_v(q_v) \quad (2.7)$$

$$\mathrm{E_{rot}} = \frac{\hbar^2}{2\mathrm{I_M}}\mathrm{J(J+1)} = \mathrm{BJ(J+1)} \quad (2.10)$$

$$E_e(Q_1,\dots,Q_{N_{vib}}) \cong E_e(Q_1^0,Q_2^0,\dots,Q_{N_{vib}}^0) + \frac{1}{2}\sum_i\frac{\partial^2E_e}{\partial Q_i^2}(Q_i-Q_i^0)^2 \quad (2.11)$$

$$E_{vib} = \hbar\sum_i\omega_i\left(v_i+\frac{1}{2}\right) \quad (2.12)$$

$$E_{vib} = \hbar\sum_i\omega_i\left(v_i+\frac{1}{2}\right) - \hbar\sum_i\omega_ix_{ie}\left(v_i+\frac{1}{2}\right)^2 \quad (2.12)$$

$$E_{el}:E_{vib}:E_{rot}\sim 1:\sqrt{\frac{m_e}{M_N}}:\frac{m_e}{M_N} \quad (2.13)$$

$$E = E_{el}(R) + \hbar\omega_e\left(v+\frac{1}{2}\right) + B_{rot}J(J+1) \quad (2.14)$$

$$i\hbar\frac{\partial\Psi}{\partial t} = \widehat{H}\Psi \quad (5.1)$$

$$\boxed{\hbar\omega_0 = E_k - E_i} \tag{5.2}$$

$$\boxed{w_{ik} = \frac{2\pi}{3\hbar^2 c g_k}(\vec{\mu}_{ik})^2 \rho_\omega} \tag{5.3}$$

$$\boxed{w_{ik} = B_{ik}\rho_\omega} \tag{5.4}$$

$$\boxed{w_{ki} = A_{ki} + B_{ki}\rho_\omega} \tag{5.5}$$

$$\boxed{A_{ki} = \frac{2\hbar\omega^3}{\pi c^2} B_{ki} \; and \; B_{ki} = B_{ik}\frac{g_i}{g_k}} \tag{5.6}$$

$$\boxed{I_\omega = N_\omega c \quad \left[\frac{photons}{m^2 s}\right]} \tag{5.7}$$

$$\boxed{I = \hbar\omega N_\omega c \quad \left[\frac{W}{m^2}\right]} \tag{5.8}$$

$$\boxed{\nu = \frac{c}{\lambda}} \tag{5.9}$$

$$\boxed{\tilde{\nu} = \frac{1}{\lambda} = \frac{c}{\nu}} \tag{5.10}$$

$$\boxed{\sigma_{ik} = \frac{B_{ik}}{c}\hbar\omega_{ki}} \tag{5.11}$$

$$\boxed{I_\omega(x) = I_\omega(0)\, exp(-\sigma_{ik} N_i x)} \tag{5.12}$$

$$\boxed{I_\omega(x) = I_\omega(0) exp(-k_{ik} x)} \tag{5.13}$$

$$\boxed{N_i = N\frac{g_i\, exp\left(-\frac{E_i}{kT}\right)}{Z(T)}} \tag{5.14}$$

$$\boxed{Z(T) = \sum_i g_i\, exp\left(-\frac{E_i}{kT}\right)} \tag{5.15}$$

$$\boxed{Z(T) = Z_{rot}(T) \cdot Z_{vib}(T) \cdot Z_{el}(T)} \tag{5.16}$$

$$\boxed{Z_{rot}(T) = \sum_j (2j+1)e^{-\frac{Bj(j+1)}{kT}} \cong \int 2xe^{-Bx^2} dx = \frac{kT}{B}} \tag{5.17}$$

$$\boxed{N_{vJ} = N_v(2j+1)\frac{B}{kT}\, exp\left(-\frac{Bj(j+1)}{kT}\right)} \tag{5.18}$$

$$\boxed{Z_{vib}(T) = \sum_n e^{-\frac{\hbar\omega_{vib} n}{kT}} = \frac{1}{1-exp\left(-\frac{\hbar\omega}{kT}\right)}} \tag{5.19}$$

$$N_v = N_e\, exp\left(-\frac{\hbar\omega_{vib}n}{kT}\right)\left(1 - exp\left(-\frac{\hbar\omega_{vib}}{kT}\right)\right) \tag{5.20}$$

$$k_{ik}(\omega) = K_{ik}L_\omega(\omega) \tag{5.21}$$

$$I_\omega(\omega) = \frac{2\pi}{\lambda^2} I_\lambda(\lambda) = 2\pi c I_{\tilde{\nu}}(\tilde{\nu}) \tag{5.22}$$

$$L(\omega) \;=\frac{2\Delta\omega_n}{\pi}\frac{1}{4(\omega-\omega_{ki})^2+\Delta\omega_n{}^2} \tag{5.23}$$

$$\Delta\omega_n = \frac{1}{\tau_k} = \sum_i A_{ki} \tag{5.24}$$

$$L(\omega) = \frac{2}{\Delta\omega_D}\sqrt{\frac{ln\,2}{\pi}}\, exp\left(-4\, ln\, 2\left(\frac{\omega-\omega_0}{\Delta\omega_D}\right)^2\right) \tag{5.25}$$

$$\Delta\omega_D = 2\frac{\omega_0}{c}\sqrt{\frac{(2\, ln\, 2)RT}{M}} \tag{5.26}$$

$$\begin{gathered} L(\omega) = \int_{-\infty}^{\infty} L_L(\omega')L_D(\omega-\omega')\, d\omega' \\ = \frac{4\Delta\omega_L}{\pi\Delta\omega_D}\sqrt{\frac{ln\,2}{\pi}}\int_{-\infty}^{\infty}\frac{1}{4(\omega'-\omega-\omega_0)^2+\Delta\omega_L{}^2}\, exp\left(-4\, ln\, 2\left(\frac{\omega'-\omega_0}{\Delta\omega_D}\right)^2\right) d\omega' \end{gathered} \tag{5.27}$$

$$\hbar\omega = E' - E'' = E_e' + E_{vib}' + E_{rot}' - E_e'' - E_{vib}'' - E_{rot}'' \tag{6.1}$$

$$\tilde{\nu} = E_{rot}' - E_{rot}'' = BJ'(J'+1) - BJ''(J''+1) \tag{6.2}$$

$$\tilde{\nu} = B(J+1)(J+2) - BJ\,(J+1) = 2B(J+1) \tag{6.3}$$

$$\begin{gathered} \tilde{\nu} = E_{vib}' + E_{rot}' - E_{vib}'' - E_{rot}'' = \tilde{\nu}_0\left(v' + \frac{1}{2}\right) + BJ'(J'+1) - \\ \tilde{\nu}_0\left(v'' + \frac{1}{2}\right) - BJ''(J''+1) \end{gathered} \tag{6.4}$$

$$\tilde{\nu}_P = \tilde{\nu}_0 + \; B(J-1)J - BJ(J+1) = \tilde{\nu}_0 - 2BJ \tag{6.5}$$

$$\tilde{\nu}_R = \tilde{\nu}_0 + B(J+1)(J+2) - BJ\,(J+1) = \tilde{\nu}_0 + 2B + 2BJ \tag{6.6}$$

$$S_{ik} = \frac{h\tilde{\nu}}{c}\frac{N_i}{N}\left(1 - \frac{g_i}{g_k}\frac{N_k}{N_i}\right)B_{ik} \tag{6.7}$$

$$S_{ik}(T) = S_{ik}(T_{ref})\frac{Z(T_{ref})}{Z(T)}\frac{exp\left(-\frac{c_2E_i}{T}\right)}{exp\left(-\frac{c_2E_i}{T_{ref}}\right)}\frac{\left(1-exp\left(-\frac{c_2\tilde{\nu}_{ik}}{T}\right)\right)}{\left(1-exp\left(-\frac{c_2\tilde{\nu}_{ik}}{T_{ref}}\right)\right)} \tag{6.8}$$

$$k_{ik}(\tilde{\nu}, P, T) = S_{ik}(T) L_{\tilde{\nu}}(\tilde{\nu}, P, T) N \quad (6.9)$$

$$k(\tilde{\nu}, P, T) = \sum_j S_j(T) L_{j,\tilde{\nu}}(\tilde{\nu}, P, T) \frac{X_j P}{kT} \quad (6.10)$$

$$\Delta\tilde{\nu}_L = \left(\frac{T_{ref}}{T}\right)^n \left(\gamma_{air}(1 - X_j) + \gamma_{self} X_j\right) P \quad (6.11)$$

$$N = \frac{1}{S_{ik}(T) L_{\tilde{\nu}}(\tilde{\nu}, P, T) l} \ln\left(C \frac{I_2}{I_1}\right) \quad (6.12)$$

$$N = \frac{\delta\tilde{\nu}}{S_{ik}(T) l} \sum_i ln\left(C \frac{I_2(\tilde{\nu}_i)}{I_1(\tilde{\nu}_i)}\right) \quad (6.13)$$

$$N = AS + B \quad (6.14)$$

$$N_{lim} = \frac{1}{S_{ik} L_\nu l} \sqrt{\left(\frac{\delta I_2}{I_2}\right)^2 + \left(\frac{\delta I_1}{I_1}\right)^2} \quad (6.15)$$

$$\begin{aligned} \frac{dN_k}{dt} &= \frac{B_{ik}}{c} I_\nu N_i - \frac{B_{ki}}{c} I_\nu N_k - (A_{ki} + Q_{ki}) N_k \\ \frac{dN_i}{dt} &= -\frac{B_{ik}}{c} I_\nu N_i + \frac{B_{ki}}{c} I_\nu N_k + (A_{ki} + Q_{ki}) N_k \end{aligned} \quad (7.1)$$

$$N_k(t) = \frac{B_{ik}}{c} I_\nu N_0 \tau \left(1 - e^{-\frac{t}{\tau}}\right) \quad (7.2)$$

$$N_k = \frac{B_{ik}}{c} I_\nu N_0 \tau = N_0 \frac{B_{ik}}{B_{ik} + B_{ki}} \frac{1}{1 + \frac{I_\nu^{sat}}{I_\nu}} = N_0 \frac{g_k}{g_k + g_i} \frac{1}{1 + \frac{I_\nu^{sat}}{I_\nu}} \quad (7.3)$$

$$I_\nu^{sat} = \frac{(A_{ki} + Q_{ki}) c}{B_{ik} + B_{ki}} \quad (7.4)$$

$$\begin{aligned} N_k &= \frac{\frac{N_0 B_{ik}}{c} I_\nu}{A_{ki} + Q_{ki}} = \frac{N_0 g_k}{g_k + g_i} \frac{I_\nu}{I_\nu^{sat}}, \quad && I_\nu \ll I_\nu^{sat} \\ N_k &= \frac{N_0 g_k}{g_k + g_i}, && I_\nu \gg I_\nu^{sat} \end{aligned} \quad (7.5)$$

$$I_{fl} = A_{ik} N_k \Delta V \frac{\Omega}{4\pi} \quad (7.6)$$

$$I_{fl} = \eta\epsilon A_{ik} N_k l S \frac{\Omega}{4\pi} \quad (7.7)$$

$$I_{fl} = \eta\epsilon \frac{\Omega}{4\pi} l S \frac{A_{ki}}{A_{ki} + Q_{ki}} \frac{N_0 B_{ik}}{c} I_\nu = \eta\epsilon \frac{\Omega}{4\pi} l S \frac{I_\nu}{I_V^{sat}} \frac{N_0 g_k}{g_i + g_k} A_{ki} \text{ (linear)} \quad (7.7)$$

$$I_{fl} = \eta\epsilon \frac{\Omega}{4\pi} l S \frac{N_0 g_k}{g_i + g_k} A_{ki} \text{ (saturation)} \quad (7.8)$$

$$N_{lim}^{sat} = \frac{1}{\eta\epsilon\frac{\Omega}{4\pi}lS\frac{g_k}{g_k+g_i}A_{ki}\Delta t} \tag{7.9}$$

$$I_{v,free}^{sat} = \frac{A_{ki}c}{B_{ik}(1+g_i/g_k)} = \frac{8\pi hc}{\lambda^3}\frac{g_k}{g_i+g_k} \tag{7.10}$$

$$I_v^{sat} = I_{v,free}^{sat}\frac{Q_{ik}}{A_{ik}} \tag{7.11}$$

$$\frac{dN_k}{dt} = \frac{B_{ik}}{c}I_vN_i - \frac{B_{ki}}{c}I_vN_k + \sum_{j\neq k}Q_{jk}N_j - N_k\sum_{j\neq k}\left(Q_{kj}+A_{kj}\right) - N_kW_k \tag{7.12}$$

$$\frac{dN_k}{dt} = \frac{\frac{B_{ik}}{c}I_vN_0e^{-\frac{E_i}{kT}}}{Z(T)} - N_k(Q_k + A_k) \tag{7.13}$$

$$S_{fl} = \int_0^{t_s} I_{fl}(t)dt = \eta\epsilon A_{ki}\frac{\Omega}{4\pi}lS\int_0^{t_s} N_k(t)dt = \eta\epsilon A_{ki}\frac{\Omega}{4\pi}l\frac{\frac{B_{ik}}{c}N_0e^{-\frac{E_i}{kT}}E_l}{Z(T)(Q_k+A_k)\Delta v_l} \tag{7.14}$$

$$N_0 = N_{cal}\frac{S_{fl}}{S_{fl}^{cal}}\frac{E_l^{cal}}{E_l} \tag{7.15}$$

$$N_0 = N_{cal}\frac{S_{fl}}{S_{fl}^{cal}}\frac{E_l^{cal}}{E_l}e^{-\frac{E_i}{k}\left(\frac{1}{T_{cal}}-\frac{1}{T}\right)}\frac{Z(T)}{Z(T_{cal})}\frac{Q_k+A_k}{Q_{k,cal}+A_k} \tag{7.16}$$

$$\rho = \rho_pVN \tag{13.1}$$

$$\phi = VN \tag{13.2}$$

$$dN = n_d\left(d_p,\vec{r},t\right)d\left(d_p\right) \tag{13.3}$$

$$\int_0^\infty n_d\left(d_p,\vec{r},t\right)d\left(d_p\right) = N \tag{13.4}$$

$$\overline{d_p} = \frac{1}{N}\int_0^\infty d_pn_d\left(d_p,\vec{r},t\right)d\left(d_p\right) \tag{13.5}$$

$$A = \int_0^\infty \pi d_p^2n_d\left(d_p,\vec{r},t\right)d\left(d_p\right) \tag{13.6}$$

$$\phi = \int_0^\infty \pi\frac{d_p^3}{6}n_d\left(d_p,\vec{r},t\right)d\left(d_p\right) \tag{13.7}$$

$$I = \frac{I_0F(\theta,\phi,\lambda)}{\left(\frac{2\pi r}{\lambda}\right)^2} \tag{13.8}$$

$$\sigma_{sc} = \left(\frac{\lambda}{2\pi}\right)^2 \int_0^{2\pi} \int_0^{\pi} F(\theta, \phi, \lambda) \sin\theta \, d\theta \, d\phi \tag{13.9}$$

$$Q_{sc} = \frac{\sigma_{sc}}{s_g} \tag{13.10}$$

$$Q_{sc} = \frac{\int_0^{2\pi} \int_0^{\pi} F(\theta,\phi,\lambda) \sin\theta \, d\theta \, d\phi}{\left(\frac{2\pi}{\lambda}\right)^2 s_g} \tag{13.11}$$

$$Q_{ext} = Q_{sc} + Q_{abs} \tag{13.12}$$

$$\vec{p} = \alpha \vec{E} \tag{13.13}$$

$$I = (1 + \cos^2\theta) \frac{k^4 \alpha^2}{2r^2} I_0 \tag{13.14}$$

$$\alpha = \frac{3}{4\pi} \frac{(m^2-1)}{m^2+2} V \tag{13.15}$$

$$Q_{sc} = \frac{8}{3} x^4 \frac{m^2-1}{m^2+2} \tag{13.16}$$

$$\begin{gathered} m = n - in' \\ n^2 - n'^2 = \epsilon \\ nn' = \frac{\lambda\sigma}{c} \end{gathered} \tag{13.17}$$

$$\mathrm{Q_{sc}} = \frac{8}{3} \mathrm{x}^4 \mathrm{Re}\left(\frac{\mathrm{m}^2-1}{\mathrm{m}^2+2}\right) \tag{13.18}$$

$$Q_{abs} = -4x Im\left(\frac{m^2-1}{m^2+2}\right) \tag{13.19}$$

$$P_{sc} = \frac{\pi d_p^2}{4} Q_{sc} N_p \Delta V I_0 \tag{13.20}$$

$$P_{sc} = \int_0^{\infty} \frac{\pi d_p^2}{4} Q_{sc}(d_p) n_p(d_p) \, d(d_p) \, \Delta V \tag{13.21}$$

$$dI = -I \left[\int_0^{\infty} \frac{\pi d_p^2}{4} Q_{ext}(d_p) n_p(d_p) \, d(d_p)\right] dx \tag{13.22}$$

$$k(x) = \int_0^{\infty} \frac{\pi d_p^2}{4} Q_{ext}(d_p) n_p(d_p) \, d(d_p) \tag{13.23}$$

$$I = I(0) e^{-\kappa L} = I(0) e^{-L \int_0^{\infty} \frac{\pi d_p^2}{4} Q_{ext}(d_p) n_p(d_p) \, d(d_p)} \tag{13.24}$$

$$k = \int_{-\infty}^{\infty} \frac{d\kappa}{d \log d_p} d \log d_p \tag{13.25}$$

$$\frac{d\kappa}{d \log d_p} = \frac{3}{2} \frac{Q_{ext}}{d_p} n_p(d_p) \frac{dV}{d \log d_p} \tag{13.26}$$