Physical Chemistry I

I – a

Write or draw appropriate words (for F, G, H), numbers (B, C, D), or figures (A, E, I, J) to fill the blanks [A] to [J] in the following sentences. Refractive index of the air is assumed to be 1.0. For [D], describe the process of calculation to derive the answer. The significant digit should be 4.

Acetylene (ethyne, C_2H_2) is a centrosymmetric linear molecule. The structural formula can be drawn as [A]. This molecule has [B] vibrational modes, which includes [C] pairs of doubly degenerate vibrational modes. When the Raman spectrum of acetylene was measured using an excitation light source with a wavelength of 500.0 nm, Raman scattering peaks were observed at 601.4, 554.8, and 518.9 nm. The Raman scattering peak at 554.8 nm corresponds to the intramolecular vibrational frequency (wavenumber) of [D] cm^{-1}. This vibrational mode is schematically drawn as [E], and is attributed to a [F] vibrational mode. The Raman scattering at 601.4 and 518.9 nm are attributable to [G] and [H] vibrational modes, respectively, which are schematically drawn as [I] and [J].

I – b

Raman scattering spectrum of a dye molecule P in solution was recorded using an excitation light source with a wavelength λ that the molecule P absorbs. The excitation light uniformly illuminated the sample solution. A strong Raman scattering band was observed at a wavelength λ_R, whose intensity was found to decrease with time. When the incident light power was 100 mW, it took 50 seconds to decrease the Raman intensity at λ_R by half. When the incident light power was 50 mW, the half-value period of the Raman intensity was 100 seconds. The half-value period of the Raman intensity was unchanged when the concentration of the molecule P was increased to twice, both for 100 mW and 50 mW cases. The Raman scattering intensity R is assumed to be proportional to the concentration of the molecule P, [P], and the incident light intensity I (the proportionality coefficient is given as σ). Answer the following questions.

(1) What is the reason why the Raman scattering intensity of the molecule P decreases with time?

(2) Write reaction rate equations for the concentration [P] under the incident powers of 100 mW and 50 mW. The rate constants for incident light powers of 100 mW and 50 mW should be denoted as $k(100)$ and $k(50)$, respectively.

(3) Find the value of $k(100)$ and $k(50)$. The significant digit should be 2. An appropriate unit should be attached. The value $\log_e 2 = 0.69$ can be used if necessary.

(4) Describe presumed relation between the reaction rate constant k and the incident light power I. Write a presumed functional form of $k(I)$.

(5) Based on the answers to questions (2) and (4), derive a differential equation for Raman scattering intensity R with respect to time, and solve it to obtain a formula that gives the time dependence of R. The formula should include σ and I as parameters. The initial concentration of P in the solution is denoted as $[P]_0$. Draw rough sketches of $R(t)$ at $I = 100$ mW and 25 mW in one graph.

Physical Chemistry II

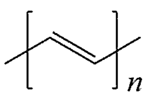
Answer all questions on electrons in solid state.

II－a

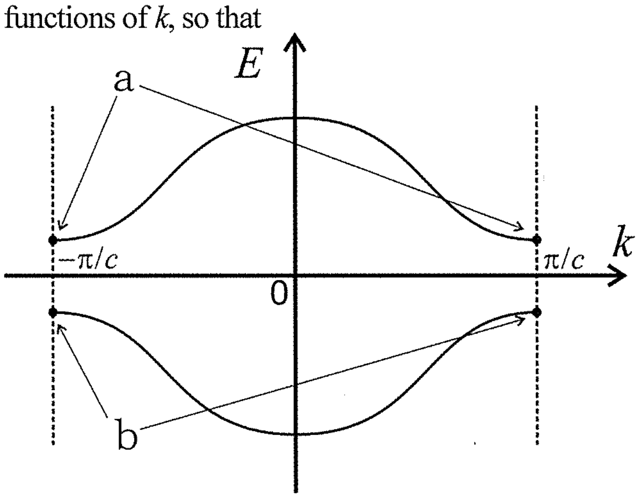
Explain difference between a metal and a semiconductor based on energy band theory.

II－b

All the electrons in bands possess their energy E that is dependent on wavenumber k ($= p/\hbar$, where p is momentum and $\hbar$ is reduced Planck constant), and the relationship between E and k is called band dispersion. For example, conduction- and valence-bands of polyacetylene exhibit band dispersions such as below, when carbon $2p_z$ orbital energy is assumed to be zero. Here, c is the lattice constant. Note that the band dispersions are periodic functions of k, so that only the dispersions corresponding to k from $-\pi/c$ to π/c are shown. The outer parts are omitted for clarity. One-dimensional electron system can be assumed in the following questions.



Polyacetylene



(1) Effective mass m of electron is given by

$$m = \frac{\hbar^2}{\left(\dfrac{\partial^2 E}{\partial k^2}\right)} \qquad \text{(eq. 1)} \ .$$

Explain the relationship between effective mass at point a (m_a) and that at point b (m_b). Assume that the conduction band and the valence band are related by mirror symmetry (with respect to k-axis).

(2) Equation of motion of electron is given by

$$m\left(\frac{d\vec{v}}{dt} + \frac{\vec{v}}{\tau}\right) = -e\vec{E} \qquad \text{(eq. 2)} \ .$$

Calculate the terminal speed v_t of an electron whose initial velocity is 0, after being placed in a static electric field $\vec{E}$ for sufficiently long time. Calculate the electron mobility $\mu = |v_t / |\vec{E}||$, too. Note that $\vec{v}$, $\tau\ (> 0)$, and $e\ (> 0)$ are velocity, relaxation time, and elemental charge, respectively.

(3) Explain how an electron at point b behaves, in comparison to that at point a.

II − c

Explain a change of electrical conductivity that is expected to occur when polyacetylene is doped with slight amount of bromine. Organic reactions such as addition reaction can be ignored.