

układ współrzędnych normalnych

$$T = \frac{1}{2} \sum_i^{3N-6} \dot{Q}_i^2 \quad V = \frac{1}{2} \sum_i^{3N-6} \lambda_i Q_i^2$$

$$H = T + V = \sum_i \left(\frac{1}{2} \dot{Q}_i^2 + \frac{1}{2} \lambda_i Q_i^2 \right)$$

$$\left(-\frac{\hbar^2}{2} \sum_i \frac{\partial^2}{\partial Q_i^2} + \frac{1}{2} \sum_i \lambda_i Q_i^2 \right) \Psi = E \Psi$$

$$\Psi = \prod_{k=1}^{3N-6} \psi_{i_k}(Q_k)$$

$$E = \sum_{k=1}^{3N-6} \left(\nu_k + \frac{1}{2} \right) h \nu_k$$

- Reguły wyboru

$$\Delta \nu_i = \pm 1, \pm 2, \dots$$

$$H_2O \quad \nu_1, \nu_2, \nu_3$$

$$C_2H_2 \quad \nu_3, \nu_5$$

$$Q_i \xrightarrow{0} \pm Q_i$$

$\times \nu_2$

$$\nu_1 - A_1, \quad \nu_2 - A_1, \quad \nu_3 - B_2$$

$$\Psi_v^i(Q_i) = N_v^i H_v(Q_i) e^{-\frac{1}{2} \frac{Q_i^2}{\alpha_i}}$$

$$\alpha_i = \frac{\hbar}{2\pi\nu_i}$$

$$\Psi_{000}(Q_1 Q_2 Q_3) = \frac{1}{(\pi^3 \alpha_1 \alpha_2 \alpha_3)^{1/4}} e^{-\frac{1}{2} \left(\frac{Q_1^2}{\alpha_1} + \frac{Q_2^2}{\alpha_2} + \frac{Q_3^2}{\alpha_3} \right)} \times Y_2 - (000)$$

A_1

$$\Psi_{100}(Q_1 Q_2 Q_3) = \frac{2}{(\alpha_1^3 \alpha_2 \alpha_3 \pi^3)^{1/4}} Q_1 e^{-\frac{1}{2} \left(\frac{Q_1^2}{\alpha_1} + \frac{Q_2^2}{\alpha_2} + \frac{Q_3^2}{\alpha_3} \right)} \times Y_2 - (100)$$

A_1

stan wzb. zlozony

$$\Psi = \prod_i \Psi_i(Q_i)$$

$$\Gamma(\Psi) = \prod_i \Gamma(\Psi_i)$$

$\times Y_2$

$$\Psi_{111} = \Psi_1(Q_1) \cdot \Psi_2(Q_2) \cdot \Psi_2(Q_3)$$

$$A_1 \times A_1 \times B_2 = B_2$$

$$R^{N'N''} = \int \Psi_{N'}^* \mu \Psi_{N''} d\tau$$

$$\Gamma(\Psi_{N'}) \times \Gamma(\mu) \times \Gamma(\Psi_{N''})$$

$$\Gamma(\mu_i) = \Gamma(\tau_i) \quad i = x, y, z$$

$$\Gamma(\Psi_{N'}) \times \Gamma(\tau_i) \times \Gamma(\Psi_{N''})$$

$\Gamma(\Psi_{N''})$ - stan podstawowy
(symetryczna)

$$\Gamma(\Psi_{N'}) = \Gamma(\tau_i) \quad i = x, y, z$$

$\times \Psi_2$

$$\Gamma(\mu_x) = B_1, \quad \Gamma(\mu_y) = B_2, \quad \Gamma(\mu_z) = A_1$$

$$A_1 \rightarrow B_1, \quad \underline{A_1 \rightarrow B_2}, \quad \underline{A_1 \rightarrow A_1}$$

- przejścia oscylacyjno-rotacyjne

$$S = F\nu_i + G(\nu_i)$$

$$G(\nu_i) = \omega_i \left(\nu_i + \frac{d_i}{2} \right)$$

= cząsteczki liniowe

$$D_{\infty h}, C_{\infty v} \quad \left\{ \Sigma, \Pi, \Delta, \dots \right\}$$

$$\Sigma \rightarrow \Sigma, \quad \Sigma \rightarrow \Pi$$

$$\Delta J = \pm 1 \quad \Sigma \rightarrow \Sigma$$

$$\Delta J = 0, \pm 1 \quad \Sigma \rightarrow \Pi$$

przejścia ramanowskie

$$\Delta J = 0, \pm 2 \quad \Sigma \rightarrow \Sigma$$

$$\Delta J = 0, \pm 1, \pm 2 \quad \Sigma \rightarrow \Pi$$

$$A_1 \rightarrow A_1, \quad A_2 \rightarrow E$$



$$\Delta K = 0, \quad \Delta J = \pm 1 \quad \text{dla } K = 0$$

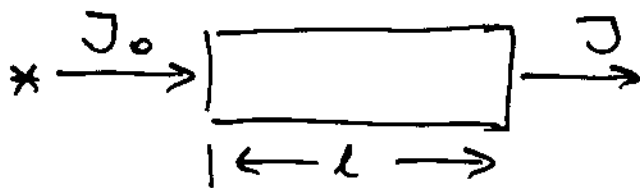
$$\Delta K = 0, \quad \Delta J = 0, \pm 1 \quad \text{dla } K \neq 0$$

$$\bar{\nu} = \omega_0 + F'(J, K) - F''(J, K)$$

$$K \leq J \quad \text{podpasma}$$

$$\begin{aligned} \bar{\nu}_0^S &= \omega_0 + F'(0, K) - F''(0, K) = \\ &= \omega_0 + [(A' - A'') - (B' - B'')] K^2 \end{aligned}$$

5.4. Spektrometry podczerwieni (spektrofotometry)



$$T = \frac{J}{J_0} = \exp(-\epsilon n l)$$

$$T(\bar{\nu})$$

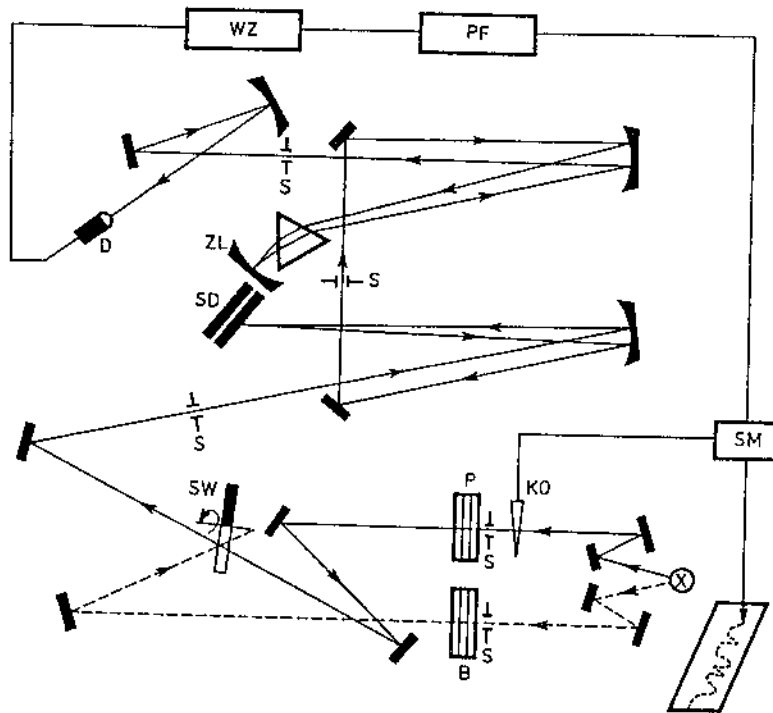
$$\epsilon n l = \ln \frac{1}{T}$$

$$\bar{A} = \int_{-\infty}^{+\infty} \epsilon d\bar{\nu}$$

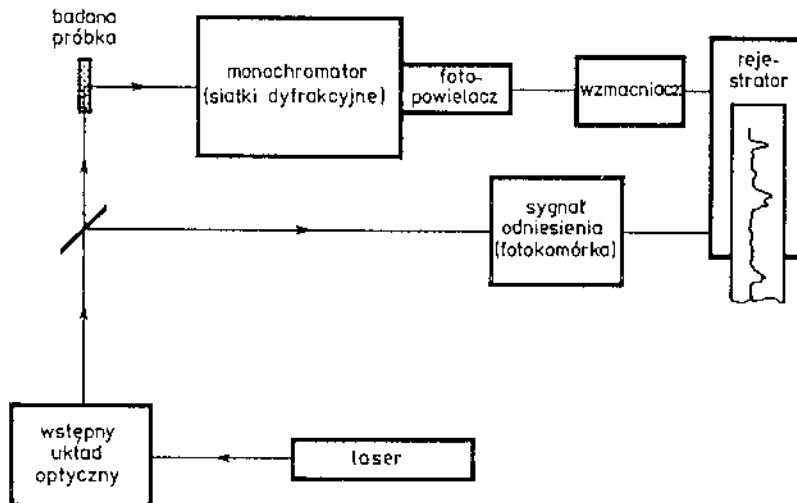
integralna
intensywność pasma

Materiały przepuszczające promieniowanie podczerwone

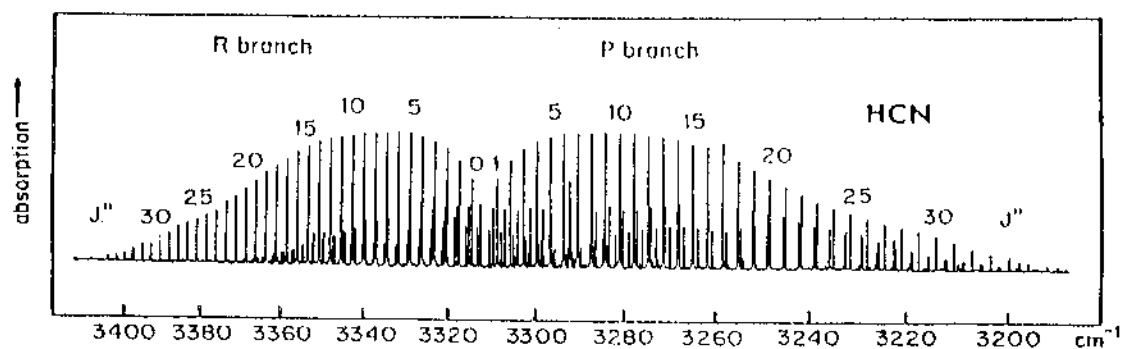
Materiał	Granica przepuszczalności		Materiał	Granica przepuszczalności	
	[μm]	[cm^{-1}]		[μm]	[cm^{-1}]
Szkło	2,5	4000	NaCl	20,0	500
Kwarc	4,4	2300	AgCl	28,0	360
Szafir	6,5	1500	KBr	32,0	310
LiF	7,0	1400	CsI	60,0	170
CaF ₂	10,0	1000	KRS-5	50,0	200



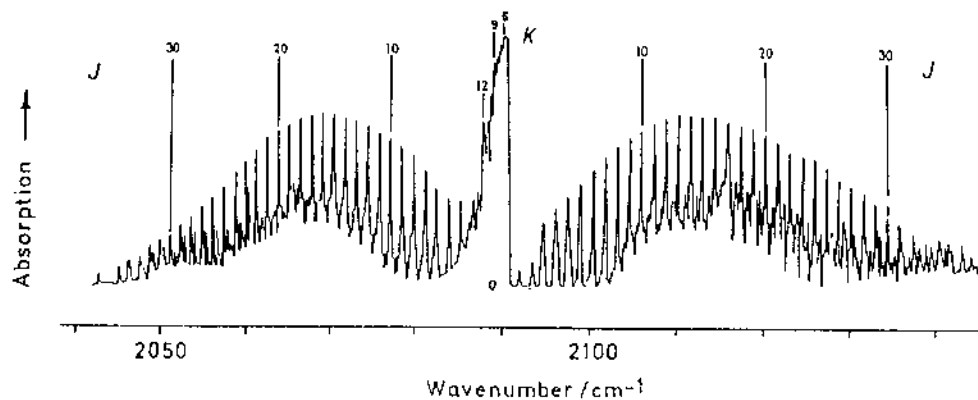
Schemat dwuwieżkowego spektrofotometru do badań podczerwieni. ⊗ – źródło promieniowania, KO – klin optyczny, P – kuweta porównawcza, B – kuweta badawcza, S – szczeliny, SW – sektor wirujący, SD – siatka dyfrakcyjna, ZL – zwierciadło Littrowa, D – detektor, WZ – wzmacniacz, PF – prostownik fazoczuły, SM – serwowymotor poruszający jednocześnie klin optyczny i piórko samopisu



Idcowy schemat spektrometru ramanowskiego



The $3_0^1, \Sigma^+ \rightarrow \Sigma^+$ infrared band of the HCN molecule showing a *P* and an *R* branch. Overlapping this is the weaker $2_{1,1}^1, \Sigma^+ \rightarrow \Sigma^+$ *H-H* hot band, the *Q* branch being at about 3292 cm^{-1} , and also the $2_2^1, \Sigma^+ \rightarrow \Sigma^+$ band with its origin at about 3290 cm^{-1} . [From Cole, A. R. H. (1977). *Tables of Wavenumbers for the Calibration of Infrared Spectrometers*, 2nd edn, p. 28. Pergamon Press, Oxford. Reproduced by permission]



The $1_{0g}, A_1 \rightarrow A_1$ vibrational infrared parallel band of the C²H₂F₂ molecule [Reproduced, with permission, from Jones, E. W., Popplewell, R. J. and Thompson, H. W. (1966). *Proc. Roy. Soc., A290*, 490]