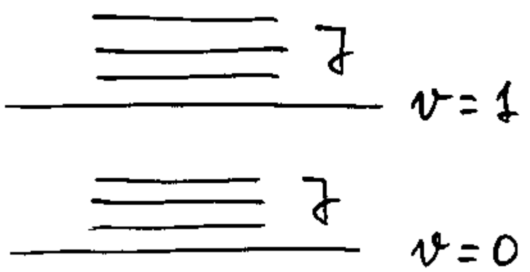
– Wpływ ruchu oscylacyjnego



$$E_v = hc\bar{\nu}\left(v + \frac{1}{2}\right)$$

$$F_v(J) = B_v J(J+1) - D_v J^2 (J+1)^2$$

$$B_v = B_e - \alpha\left(v + \frac{1}{2}\right) + \dots$$

$$D_v = D_e - \beta\left(v + \frac{1}{2}\right) + \dots$$

CS $\quad B_e = 24584$ MHz

$\alpha = 177$ MHz

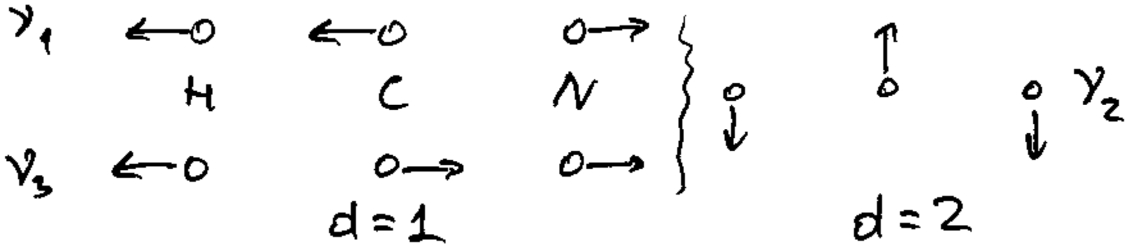
$D_e = 43$ kHz

$$\frac{N_v}{N_0} = e^{-\frac{\Delta E_v}{kT}} = e^{-\frac{hc\bar{\nu} v}{kT}}$$

$$\frac{N_v}{N_0} < 0.1 \qquad T = 293\,\mathrm{K}$$

$$B_v = B_e - \sum_i^{3N-5} \alpha_i \left(v_i + \frac{d_i}{2}\right)$$

HCN

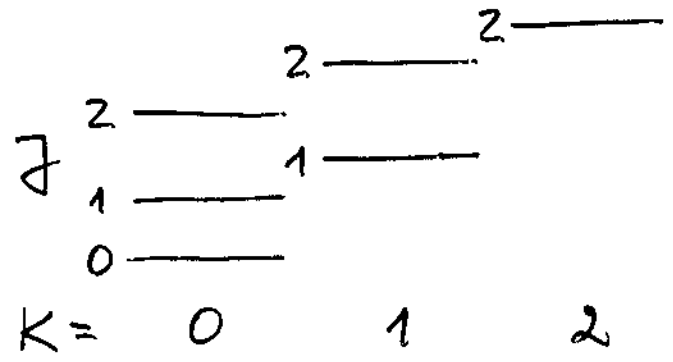


4.3 Cząsteczki typu bąk symetryczny

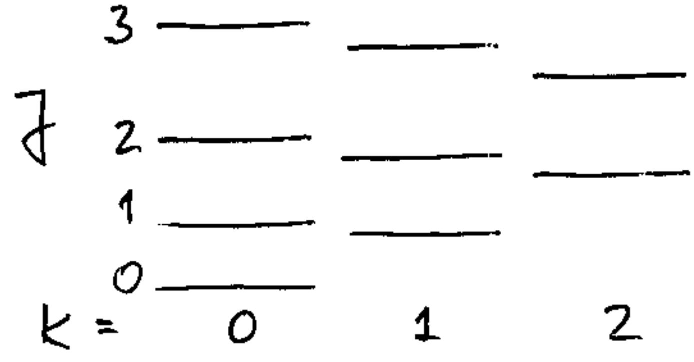
$$L_a = \hbar K \qquad K = 0, 1, 2, \ldots, J$$

$$F_v(J, K) = B_v J(J+1) + (A_v - B_v) K^2$$

$$A = \frac{\hbar^2}{2hc J_a} \qquad B = \frac{\hbar^2}{2hc J_b} \qquad A > B$$



b. s. wydłużony



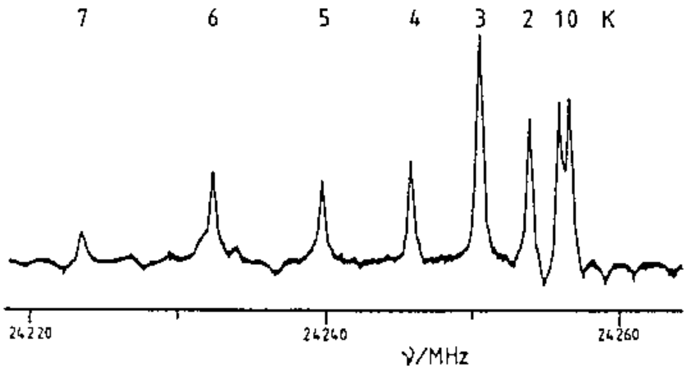
b. s. spłaszczony

$$\Delta J = \pm 1 \quad , \quad \Delta K = 0$$

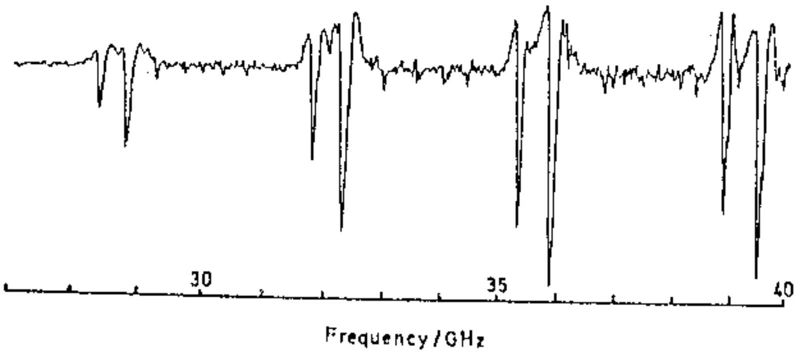
$$\bar{\nu} = F_v(J+1, K) - F_v(J, K) =$$

$$= 2B_v(J+1)$$

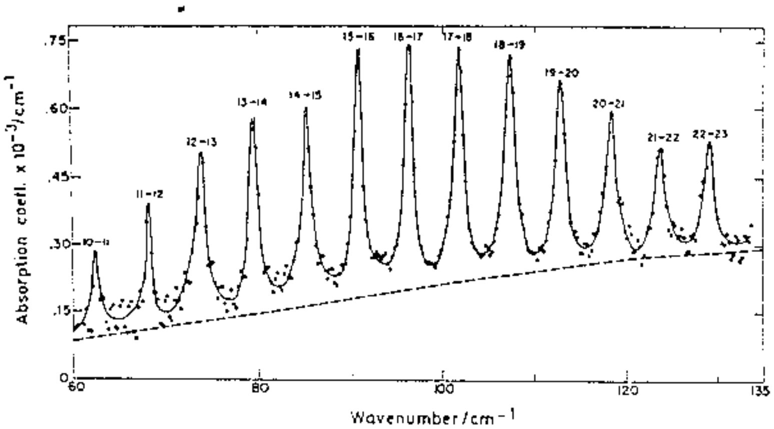
$$\bar{\nu} = 2(B_v - D_{JK}K^2)(J+1) - 4D_J(J+1)^3$$



The $J = 8$–7 microwave transition in the vibrational ground state of the SiH_3NCS molecule showing the eight components split by centrifugal distortion



Part of the microwave spectrum of the crotonic acid molecule showing two series of transitions, the weaker series due to the *s-cis* and the stronger to the more abundant *s-trans* isomer [Reproduced, with permission, from Scharpen, L. H. and Laurie, V. W. (1972). *Anal. Chem.*, **44**, 378R]



The far infrared pure rotational spectrum of the SiH_4 molecule obtained with a Michelson interferometer [Reproduced, with permission, from Rosenberg, A. and Ozier, I. (1974). *Can. J. Phys.*, **52**, 575]

$\mu \approx 8.3 . 10^{-6}$ D

4.4. Efekt Starka

$$E = -\vec{\mu} \cdot \vec{\mathcal{E}}$$

$$\mu_J = \mu \frac{K}{[J(J+1)]^{1/2}}$$

$$E^{(1)} = -\vec{\mu}_J \cdot \vec{\mathcal{E}} = -\mu_J \mathcal{E} \cos\Theta$$

$$\cos\Theta = \frac{M}{[J(J+1)]^{1/2}}$$

$$E^{(1)} = -\mu \mathcal{E} \frac{KM}{J(J+1)} \qquad (1)$$

$$E \sim \vec{\mu} \cdot \vec{\mathcal{E}} \frac{\vec{\mu} \cdot \vec{\mathcal{E}}}{hcB J(J+1)}$$

$$E^{(2)} \sim \mu^2 \frac{\mathcal{E}^2}{hcB J(J+1)} \qquad (11)$$

$$E^{(2)}_{JM} = \frac{\mu^2 \mathcal{E}^2}{2hcB} \frac{J(J+1) - 3M^2}{J(J+1)(2J-1)(2J+3)}$$

$|M| = 0, 1, 2$ $\qquad$ $(J+1)$ składowych

$$\langle J, M | \mu | J', M' \rangle \neq 0$$

$$\Delta J = \pm 1$$

$$\Delta M = 0, \pm 1$$

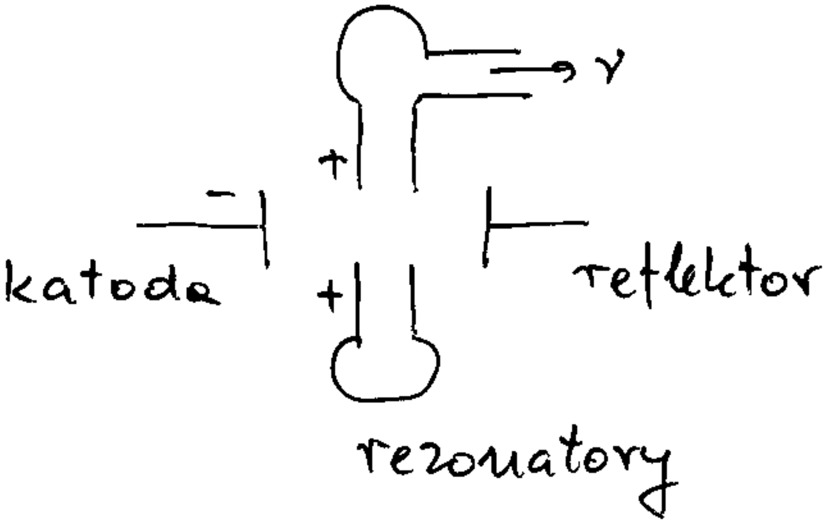
$(3J+2)$ przejścia

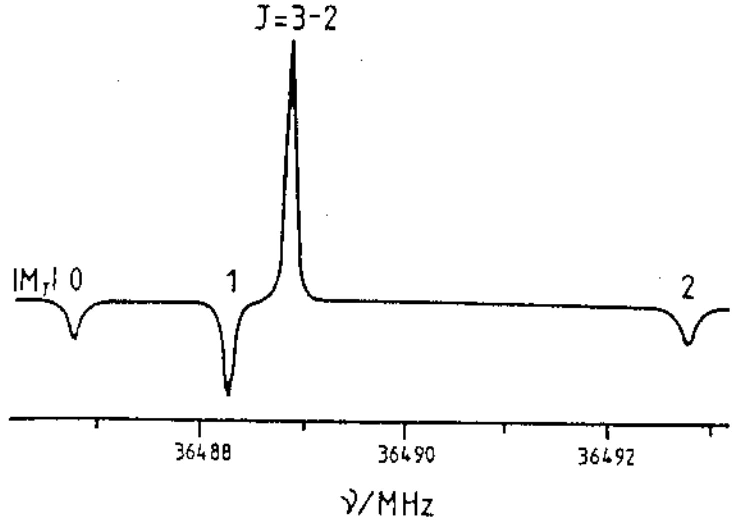
$\vec{P} \parallel \vec{\mathcal{E}} \rightarrow \Delta M = 0 \quad \vec{P} \perp \vec{\mathcal{E}} \rightarrow \Delta M = \pm 1$

OCS $\quad \mu = 0.7152 \pm 0.0002 D$

$\frac{\Delta \nu}{\nu} = 10^{-4} - 10^{-3} \quad \mathcal{E} = 10^{5} \frac{V}{m}$

4.5 Spektrometr mikrofalowy





The Stark effect on the $J=3$–2 microwave transition of the OCS molecule