5. Spektroskopia oscylacyjna

5.1 Cząsteczki dwuatomowe

$$E_v = h\nu\left(v + \frac{1}{2}\right) \qquad v = 0, 1, \ldots$$

$$\nu = \frac{1}{2\pi}\left(\frac{k}{\mu_m}\right)^{1/2}$$

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

$$R^{v'v''} = \langle v' | \mu | v'' \rangle$$

$$\mu = \mu_e + \left(\frac{d\mu}{dq}\right)_e q + \frac{1}{2!}\left(\frac{d^2\mu}{dq^2}\right)_e q^2 + \ldots$$

$$R^{v'v''} = \left(\frac{d\mu}{dq}\right)_e \langle v' | q | v'' \rangle$$

$$\Delta v = \pm 1$$

$\Delta v = \pm 1, \pm 2, \ldots$ anharmoniczność

$$G(v) = \omega_e\left(v + \frac{1}{2}\right) - \omega_e x_e\left(v + \frac{1}{2}\right)^2 + \omega_e y_e\left(v + \frac{1}{2}\right)^3 + \ldots$$

$^1H^{35}Cl$

$\omega_e = 2991\ cm^{-1}$, $\omega_e x_e = 53\ cm^{-1}$

$\omega_e y_e = 0.22\ cm^{-1}$

$$v \rightarrow v+1$$

$$\bar{\nu}(v', v'') = G(v+1) - G(v) =$$

$$= \omega_e - \omega_e x_e (2v+2) + \omega_e y_e \left(3v^2 + 6v + \frac{13}{4}\right)$$

$$D_o = \sum_v \Delta G_{v+\frac{1}{2}}$$

$$\Delta G_{v+\frac{1}{2}} = G(v+1) - G(v)$$

$$G(0) = \frac{1}{2}\omega_e - \frac{1}{4}\omega_e x_e$$

$$D_o(^2H_2) > D_o(^1H_2)$$

$$U(q) = D_e\left[1 - e^{-aq}\right]^2 \quad \text{k. Morse'a}$$

$$q = r - r_e$$

$$a = \left(\frac{2\pi^2 c \mu}{D_e h}\right)^{1/2} \omega_e$$

$$x_e = \frac{\omega_e}{4 D_e}$$

– Spektroskopia rotacyjno-oscylacyjna

$$S = G(v) + F_v(J) =$$

$$= \omega_e\left(v+\tfrac{1}{2}\right) - \omega_e x_e \left(v+\tfrac{1}{2}\right)^2 +$$

$$+ B_v J(J+1) - D_v J^2 (J+1)^2 + \ldots$$

$$\Delta J = \pm 1$$

$$B_1 = B_0 = B \qquad B' = B'' = B$$

$$\bar{\nu}[R(J)] = \omega_0 + B(J+1)(J+2) - BJ(J+1) =$$

$$= \omega_0 + 2BJ + 2B$$

$$\bar{\nu}[P(J)] = \omega_0 - 2BJ$$

$$\bar{\nu}[R(0)] - \bar{\nu}[P(1)] = 4B$$

$$\Delta_2'' F(J) = \bar{\nu}[R(J-1)] - \bar{\nu}[P(J+1)] =$$

$$= 4B''\left(J+\tfrac{1}{2}\right) \longrightarrow 4B''$$

$$\Delta_2' F(J) = \bar{\nu}[R(J)] - \bar{\nu}[P(J)] =$$

$$= 4B'\left(J+\tfrac{1}{2}\right) \longrightarrow 4B'$$

środek pasma

$$\omega_0 = \bar{\nu}[R(0)] - 2B' =$$

$$= \bar{\nu}[P(1)] + 2B''$$

$$\Delta_2^4 F(J) = (4B'' - 6D'')(J + \tfrac{1}{2}) +$$

$$- 8D''(J + \tfrac{1}{2})^3$$

$$B_0 , B_1 \rightarrow B_e , \alpha$$

– Rozpraszanie ramanowskie

$$\alpha = \alpha_e + \left(\frac{d\alpha}{dq}\right)_e q + \frac{1}{2}\left(\frac{d^2\alpha}{dq^2}\right) q^2 + \ldots$$

$$R^{v'v''} = \left(\frac{d\alpha}{dq}\right)_e \langle v' | q | v'' \rangle$$

$$\Delta v = \pm 1$$

$$\Delta J = 0, \pm 2$$

$$Q - \Delta J = 0 \quad , \quad O - \Delta J = -2 \quad , \quad S - \Delta J = 2$$

$$B' = B'' = B$$

$$\bar{\nu}[S(J)] = \omega_0 + 4B]J + 6B$$

$$\bar{\nu}[O(J)] = \omega_0 - 4B]J + 2B$$

$$\bar{\nu}[Q(J)] = \omega_0$$

$$\Delta_4'' F(J) = \bar{\nu}[S(J-2)] - \bar{\nu}[O(J+2)] =$$

$$= 8B''(J + \tfrac{1}{2})$$

$$\Delta_4' F(J) = 8B'(J + \tfrac{1}{2})$$

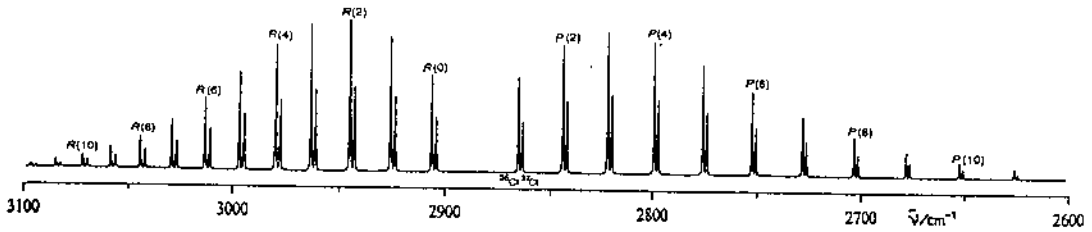
5.2. Cząsteczki wieloatomowe

$$3N-6 \quad , \quad 3N-5$$

$$G(v_i) = \omega_i (v_i + \tfrac{1}{2})$$

$$G(v_i) = \omega_i (v_i + \frac{d_i}{2})$$

$$\Delta v_i = \pm 1, \mp 2, \ldots$$

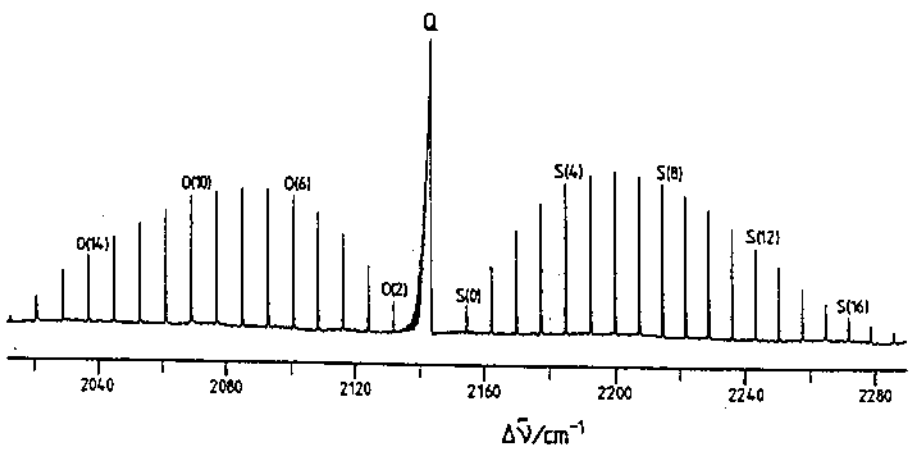


The $v = 1 - 0$ infrared spectrum of the $^1H^{35}Cl$ and $^1H^{37}Cl$ molecules showing the P- and R-branch rotational structure

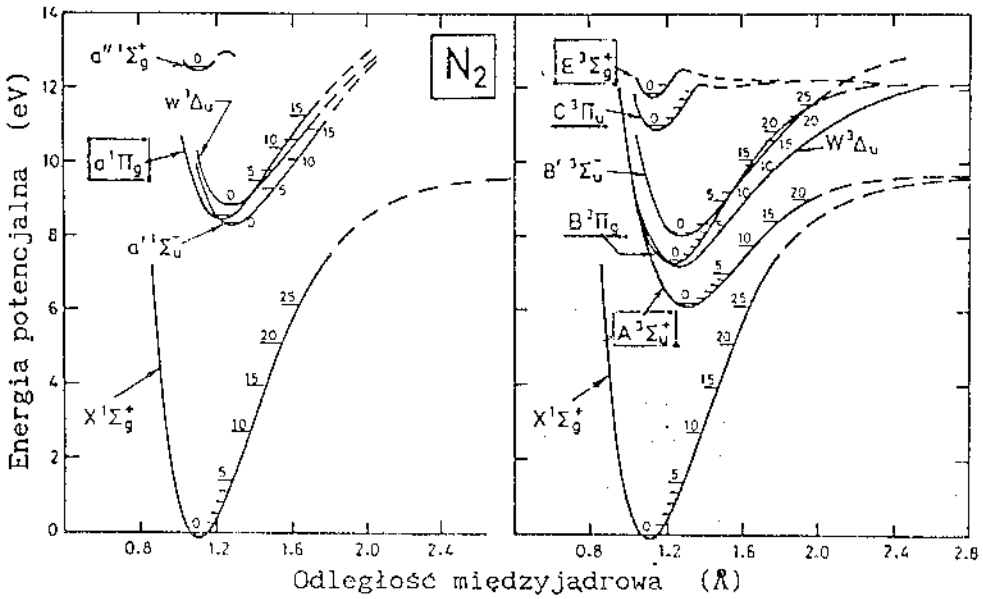
Rotational and vibrational constants for $^1H^{35}Cl$[a]

$v = 0$		$v = 1$	
B_0	10.440 254 cm^{-1}	B_1	10.136 228 cm^{-1}
D_0	5.2828×10^{-4} cm^{-1}	D_1	$5.215\,7 \times 10^{-4}$ cm^{-1}
ω_0 (for $v = 1$–0 transition)			2885.977 5 cm^{-1}
B_e			10.593 42 cm^{-1}
α_e			0.307 18 cm^{-1}

[a]Data taken from Rank, D. H., Rao, B. S. and Wiggins, T. A. (1965). *J. Mol. Spectrosc.*, 17, 122.



The $v = 1$–0 Stokes Raman spectrum of the CO molecule showing the O-, Q- and S-branch rotational structure



Stan	Energia [v = 0] (eV)
$A^3\Sigma_u^+$	6.169
$B^3\overline{\Pi}_g$	7.353
$a^1\overline{\Pi}_g$	8.549
$C^3\overline{\Pi}_u$	11.032
$E^3\overline{\Sigma}_g^+$	11.875