układ współrzędnych normalnych

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

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

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

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

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

– Reguły wyboru

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

H_2O $\qquad\qquad$ ν_1, ν_2, ν_3

C_2H_2 $\qquad\qquad$ ν_3, ν_5

$$Q_i \xrightarrow{O} \pm Q_i$$

XY_2

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

$$(g_{11} g_{22} - g_{12} g_{21}) \lambda^2 - (g_{11} f_{22} + f_{11} g_{22}) \lambda +$$
$$+ f_{11} f_{22} = 0$$

HCN

$m_A = 1$ a.u. $\quad m_B = 12$ a.u. $\quad m_C = 14$ a.u.

$M = 27$ a.u. $\qquad 1 \text{ a.u.} = 1.66 \cdot 10^{-27}$ kg

$g_{11} = 0.96$ a.u. $\quad g_{22} = 6.74$ a.u

$g_{12} = g_{21} = 0.52$ a.u.

$f_{11} = 5.8 \cdot 10^2 \, \frac{N}{m} \qquad f_{22} = 17.9 \cdot 10^2 \, \frac{N}{m}$

$\lambda_1 = 3.90 \cdot 10^{29} \, \frac{1}{s^2}$

$\lambda_3 = 1.56 \cdot 10^{29} \, \frac{1}{s^2}$

$\bar{\nu}_1 = 3310 \text{ cm}^{-1} \qquad \bar{\nu}_3 = 2090 \text{ cm}^{-1}$

$$\frac{A_1}{A_2} = \frac{g_{12} \lambda_1}{f_{11} - g_{11} \lambda}$$

$\nu_1 \quad A_1 : A_2 = 1 : -0.13$

$\nu_3 \quad A_1 : A_2 = 1 : 2.5$

TABLE 63

MOLECULAR CONSTANTS OF THE ELECTRONIC STATES OF TRIATOMIC MONOHYDRIDES

State	Point Group	T_0	Vibrational Frequencies ν_1	ν_2	ν_3	Rotational Constants A_0	B_0	C_0	$r_0(\mathrm{HX})$	$r_0(\mathrm{XY})$	α	Electron Configuration	Observed Transitions	References	Remarks
HCN	I.P. = 13.91 eV[a]; D(H—CN) = 5.6$_5$ eV[b]; D(HC—N) = 9.69 eV														
$\tilde{D}$		71629	Very strong unclassified diffuse bands below 1120 Å	(1038)										(1029)	Diffuse bands
$\tilde{C}\,{}^1A'$	C_s	65644	2273	869	(1530)	35.$_8$			(1.14)		141°	$\ldots(a')(a')^2(a'')^2(a')$[c]	$\tilde{C}$—$\tilde{X}$ 1550–1350 Å	(528) (528)	$\gamma-X$ system of (527) see Fig. 88
$\tilde{B}\,{}^1A''$	C_s	(54620)[d]		[728.6][d]		[12.0][d]	[1.157][d]	[1.043][d]	(1.14)	1.334	114.5°	$\ldots(a')^2(a')(a'')^2(a'')$	$\tilde{B}$←$\tilde{X}$ 1830–1535 Å	(527)	$\beta-X$ system of (527) predissociation
$\tilde{A}\,{}^1A''$	C_s	52256.4[e]		940.6	1495.$_0$	22.8	1.332	1.251	1.14$_0$	1.297	125.0°	$\ldots(a')^2(a')^2(a'')(a')$[f]	$\tilde{A}$←$\tilde{X}$ 1915–1600 Å	(527)	$\alpha-X$ system of (527), see Figs. 82 and 87, predissociation[g]
$\tilde{X}\,{}^1\Sigma^+$	$C_{\infty v}$	0	3311.47	713.46	2096.7[h]	—	1.47822[i]	—	1.064[j]	1.156[j]	180°	$\ldots\sigma^2\pi^4$	infrared and microwave sp.	(1048) (1136) (301)	
HCP															
$\tilde{D}\,{}^1\Sigma^+$	$C_{\infty v}$	40255		(615)	(970)	—	(0.61)	—			(180°)		$\tilde{D}$←$\tilde{X}$ 2490–2360 Å	(639)	
$\tilde{C}$?		35980			950								$\tilde{C}$←$\tilde{X}$ 2780–2650 Å	(639)	
$\tilde{B}\,{}^1A'$	$C_{\infty v}$	35926.3			964	—	0.600$_5$	—			180°	$\ldots\sigma^2\pi^3\pi^*$	$\tilde{B}$←$\tilde{X}$ 2780–2580 Å	(639)	
$\tilde{A}\,{}^1A''$	C_s	34769.9		566.6	950.9	~24	0.589	0.577	(1.14)	1.69	128°	$\ldots(a')^2(a')^2(a'')(a')$	$\tilde{A}$←$\tilde{X}$ 3000–2300 Å	(639)	
$\tilde{a}\,{}^3\Sigma^+$	($C_{\infty v}$)	24400	2720	440	950	—	(0.578)				(180°)		$\tilde{a}$←$\tilde{X}$ 4100–3050 Å	(639)	Extensive system of discrete bands $\lambda + \frac{1}{2}\gamma = -1.1_0$ cm^{-1}
$\tilde{X}\,{}^1\Sigma^+$	$C_{\infty v}$	0	3216.9$_0$	674.2$_5$	1278.2$_3$	—	0.66625[a]	—	1.067	1.542	180°	$\ldots\sigma^2\pi^4$	microwave and infrared sp.	(1228) (639)	

HCN: [a] From electron impact experiments of (881). [b] Using D(CN) = 7.5$_0$ eV after (112). [c] Derived from $\sigma\pi^4\pi^*$. [d] Refers to DCN since only fragments of this system have been found for HCN. [e] This is ν_0 of the 000–000 band less ($A - B$) since the upper state of this band has $K = 1$. [f] Derived from $\sigma^2\pi^3\pi^*$. [g] See Table 47. [h] Quoted without explanation by (60). (301) give from Raman measurements: 2095.5. [i] $\alpha_1 = 0.0104_2$, $\alpha_2 = -0.0036_1$, $\alpha_3 = 0.0095$, $D_{000} = 2.914 \times 10^{-6}$. [j] For r_e (301) give 1.0657 and 1.1530 Å.

HCP: [a] $\alpha_1 = 0.0031$, $\alpha_2 = -0.0003_4$, $\alpha_3 = 0.003_4$.

$$g_{11} = \frac{m_A}{M^2}\left[(m_B+m_C)^2 + m_A m_B + m_A m_C\right]$$

$$g_{12} = g_{21} = \frac{m_A m_C}{M}$$

$$g_{22} = \frac{m_C}{M^2}\left[(m_A+m_B)^2 + m_A m_C + m_B m_C\right]$$

równania Lagrange'a

$$\frac{d}{dt}\left(\frac{\partial T}{\partial \dot{\xi}_i}\right) + \frac{\partial U}{\partial \xi_i} = 0$$

$$i = 1, \ldots$$

$$\sum_j \left(g_{ij}\ddot{\xi}_j + f_{ij}\xi_j\right) = 0 \qquad i = \ldots$$

$$\xi_j = A_j^k \cos 2\pi \nu_k t$$

$$\ddot{\xi}_j = -\lambda_k \xi_j \qquad \lambda_k = 4\pi^2 \nu_k^2$$

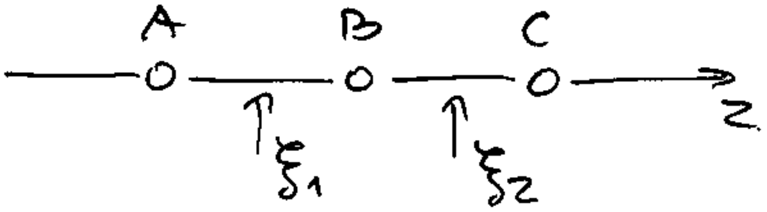
$$\sum_j \left(f_{ij} - g_{ij}\lambda_k\right) A_j^k = 0 \qquad i = \ldots$$

$$(f_{11} - g_{11}\lambda)A_1 + (f_{12} - g_{12}\lambda)A_2 = 0$$

$$(f_{21} - g_{21}\lambda)A_1 + (f_{22} - g_{22}\lambda)A_2 = 0$$

$$\begin{vmatrix} f_{11} - g_{11}\lambda & -g_{12}\lambda \\ -g_{21}\lambda & f_{22} - g_{22}\lambda \end{vmatrix} = 0$$

7. Drgania rozciągające cząsteczki ABC



$$U = \frac{1}{2} f_{11} \xi_1^2 + \frac{1}{2} f_{22} \xi_2^2$$

$$T = \frac{1}{2} m_A \dot{z}_A^2 + \frac{1}{2} m_B \dot{z}_B^2 + \frac{1}{2} m_C \dot{z}_C^2$$

$$\xi_1 = z_B - z_A \qquad \xi_2 = z_C - z_B$$

$$\dot{\xi}_1 = \dot{z}_B - \dot{z}_C$$

$$\xi_2 = \dot{z}_C - \dot{z}_B$$

$$m_A \dot{z}_A + m_B \dot{z}_B + m_C \dot{z}_C = 0$$

$$\dot{z}_A = -\frac{m_B + m_C}{M} \dot{\xi}_1 - \frac{m_C}{M} \dot{\xi}_2$$

$$\dot{z}_B = \frac{m_A}{M} \dot{\xi}_1 - \frac{m_C}{M} \dot{\xi}_2$$

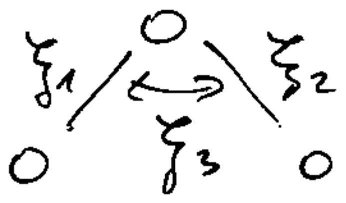
$$\dot{z}_C = \frac{m_A}{M} \dot{\xi}_1 + \frac{m_A + m_B}{M} \dot{\xi}_2$$

$$M = m_A + m_B + m_C$$

$$T = \frac{1}{2} \sum_{ij}^{2} g_{ij} \dot{\xi}_1 \dot{\xi}_2$$

5.3 Drgania normalne cząsteczek

3N − 6 współrzędnych



$$U = \frac{1}{2}\sum_{ij}^{3N-6} f_{ij}\,\xi_i\,\xi_j \qquad [F]$$

$$T = \frac{1}{2}\sum_{ij}^{3N-6} g_{ij}\,\dot{\xi}_i\,\dot{\xi}_j \qquad [G]$$

$$\frac{d}{dt}\left(\frac{\partial T}{\partial \dot{\xi}_i}\right) + \frac{\partial U}{\partial \xi_i} = 0 \qquad \text{r. Lagrange'a}$$

$$\sum_{j}^{3N-6}\left(g_{ij}\,\ddot{\xi}_j + f_{ij}\,\xi_j\right) = 0 \qquad (3N-6)\ \text{r.}$$

$$\xi_j = A_{jk}\cos 2\pi \nu_k t$$

$$\ddot{\xi}_j = -4\pi^2 \nu_k^2\,\xi_j = -\lambda_k\,\xi_j$$

$$\sum_{j}^{3N-6}\left(f_{ij} - g_{ij}\lambda_k\right)\xi_j = 0$$

$$\left|f_{ij} - g_{ij}\lambda_k\right| = 0 \qquad \left|F - G\lambda_k\right| = 0$$

r. Ramana $\quad \dfrac{\partial \alpha}{\partial q_i}$

$$\alpha_{ii} \rightarrow \left(\frac{\partial \alpha_{ii}}{\partial q_i}\right)_e$$

$$\dot{\alpha}_{śr\,j}\ ,\ \dot{\gamma}_j$$

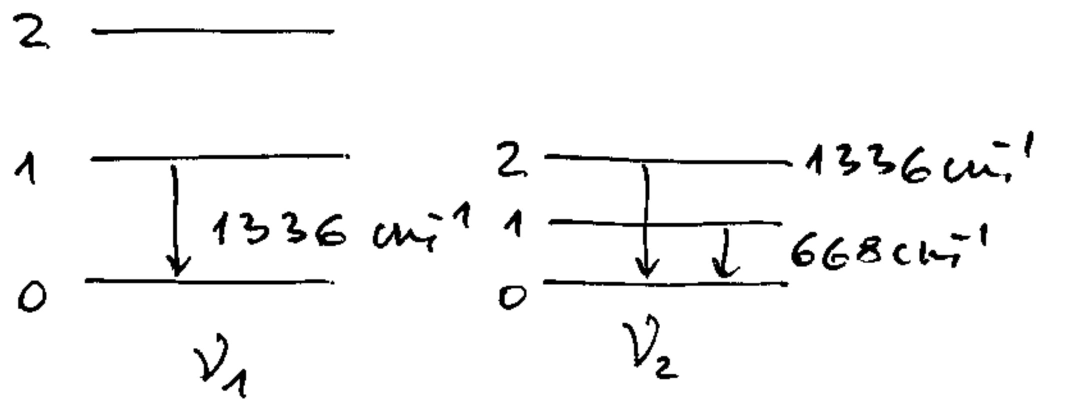
$$\rho_j^p = \frac{3\dot{\gamma}_j^2}{45\dot{\alpha}_{śr\,j}^2 + 4\dot{\gamma}_j^2}$$

$$0 \leq \rho_i^p \leq \frac{3}{4}$$

$\rho_j^p < \frac{3}{4}$ symmetryczne

$\rho_i^p = \frac{3}{4}$ asymetryczne

rezonans Fermiego



$$2\bar{\nu}_2 \simeq \bar{\nu}_1$$

1389 cm⁻¹

1286 cm⁻¹

$C-H$

C_2H_2	$\equiv C-H$	$5.85 \cdot 10^2 \frac{N}{m}$
C_2H_4	$=C\lessdot^{H}$	$5.1 \cdot 10^2 \frac{N}{m}$
CH_4	$\geq C-H$	$4.79 \cdot 10^2 \frac{N}{m}$

– Rozpraszanie ramanowskie

$$\rho^P(\theta) = \frac{J_{\parallel}(\theta)}{J_{\perp}(\theta)}$$

$\Theta = \frac{\pi}{2}$ r. Rayleigh'a

$$\rho^P = \frac{3\gamma^2}{45\alpha_{śr}^2 + 4\gamma^2}$$

$$\alpha_{śr} = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$

$$\gamma = \sqrt{\frac{1}{2}(\alpha_{xx}-\alpha_{yy})^2 + (\alpha_{yy}-\alpha_{zz})^2 + (\alpha_{zz}-\alpha_{xx})^2}$$

$$\rho = 0$$

$$\rho = \frac{1}{3}$$

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

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

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

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

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

$$= 8B''\left(J + \frac{1}{2}\right)$$

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

5.2. Cząsteczki wieloatomowe

$3N-6$, $3N-5$

$$G(v_i) = \omega_i \left(v_i + \frac{1}{2}\right)$$

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

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