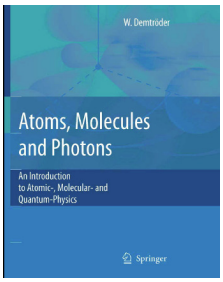
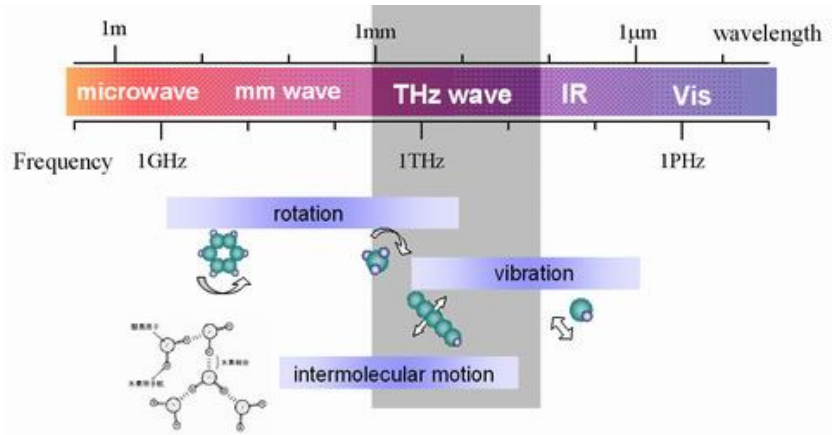
Molekulák forgó- és rezgőmozgása, vibrációs és rotációs átmenetek Kétatomos molekulák

2013. november 27.



W. Demtröder,
Atoms Molecules and Photons könyve alapján

Spektrum



Adiabatikus közelítés

Hamilton operátor

$$\hat{H} = -\frac{\hbar^2}{2}\sum_{k=1}^{2}\frac{1}{M_k}\nabla_k^2 - \frac{\hbar^2}{2m_e}\sum_{i=1}^{N}\nabla_i^2$$
$$+\frac{e^2}{4\pi\varepsilon_0}\left[\frac{Z_1 Z_2}{R} + \sum_{i,j}\frac{1}{r_{i,j}} - \sum_i\left(\frac{1}{r_{i1}}+\frac{1}{r_{i2}}\right)\right]$$
$$= \hat{E}_{\text{kin}}^{\text{nucl}} + E_{\text{kin}}^{\text{el}} + E_{\text{pot}}^{0} = \hat{T}_k + \hat{H}_0$$

Adiabatikus közelítés

$$H = H_0 + T_k$$

$$\psi(\boldsymbol{r}_i, \boldsymbol{R}_k) = \chi(\boldsymbol{R}_k)\cdot\Phi(\boldsymbol{r}_i, \boldsymbol{R}_k)$$

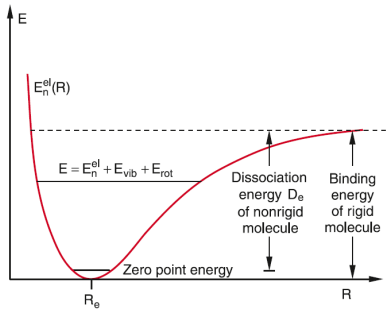
molekula állapot — magmozgás — elektron állapot

Adiabatikus közelítés

A Hamilton operátor sajátérték egyenletébe helyettesítve

$$\hat{H}_0\Phi_n^{\text{el}}(\boldsymbol{r}, \boldsymbol{R}_k) = E_n^{(0)}\cdot\Phi_n^{\text{el}}(\boldsymbol{r}, \boldsymbol{R}_k)$$
$$\left(\hat{T}_k + E_n^{(0)}\right)\chi_{n,m}(\boldsymbol{R}) = E_{n,m}\chi_{n,m}(\boldsymbol{R})$$

$$E_n^{(o)} = \left\langle E_{\text{kin}}^{\text{el}}\right\rangle + E_{\text{pot}}(\boldsymbol{r}_i, \boldsymbol{R}_k)$$



A teljes energia

$$E_{n,k} = E_{\text{kin}}^{\text{nuc}} + E_n^{(o)}$$

A magmozgásokat leíró egyenlet

$$\left[\left(\frac{-\hbar^2}{2M_A}\Delta_A - \frac{-\hbar^2}{2M_B}\Delta_B\right) + E_{\text{pot}}^{(n)}(\boldsymbol{R}_k)\right]\chi_{n,m}(\boldsymbol{R}_k)$$
$$= E_{n,m}\chi_{n,m}(\boldsymbol{R}_k)\,.$$

A magmozgásokat leíró egyenlet

Áttérés tömegközépponti koordinátákra

gömbszimmetrikus potenciál

$$\left[\frac{-\hbar^2}{2M}\Delta + E_{\text{pot}}^{(n)}(R)\right]\chi_{n,m}(R) = E_{n,m}\chi_{n,m}(R) \qquad M = M_{\text{A}}M_{\text{B}}/(M_{\text{A}}+M_{\text{B}})$$

A H-atomhoz hasonlít! → Kezeljük hasonlóan.

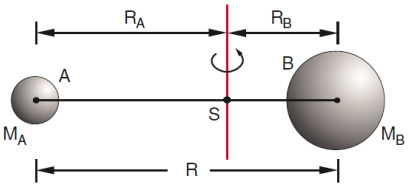
Gömbi polár $\chi(R,\vartheta,\varphi)$ Szeparáció $\chi(R,\vartheta,\varphi) = S(R)\cdot Y(\vartheta,\varphi)$

radiális fgv gömb fgv

$$\frac{1}{R^2}\frac{\mathrm{d}}{\mathrm{d}R}\left(R^2\frac{\mathrm{d}S}{\mathrm{d}R}\right) + \frac{2M}{\hbar^2}\left[E - E_{\text{pot}}(R) - \frac{J(J+1)\hbar^2}{2MR^2}\right]S = 0$$ rezgések

$$\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial Y}{\partial\vartheta}\right) + \frac{1}{\sin^2\vartheta}\frac{\partial^2 Y}{\partial\varphi^2} + J(J+1)Y = 0$$ rotáció

Merev rotor



$E_{\text{rot}} = \frac{1}{2}I\omega^2 = J^2/(2I)$

$I = M_{\text{A}}R_{\text{A}}^2 + M_{\text{B}}R_{\text{B}}^2 = MR^2$

$M = M_{\text{A}}M_{\text{B}}/(M_{\text{A}}+M_{\text{B}})$

$|J| = I\omega \qquad |J|^2 = J(J+1)h^2$

Az R_{e} egyensúlyi magtávolságra

$$E_{\text{rot}} = \frac{J(J+1)\hbar^2}{2MR_{\text{e}}^2}$$

„Kvantumos” levezetés

$$\cancel{\frac{1}{R^2}\frac{\mathrm{d}}{\mathrm{d}R}\left(R^2\frac{\mathrm{d}S}{\mathrm{d}R}\right)} + \frac{2M}{\hbar^2}\left[E - E_{\text{pot}}(R) - \frac{J(J+1)\hbar^2}{2MR^2}\right]S = 0$$

0

$E - E_{pot} = E_{kin} = E_{rot} + \cancel{E_{vib}}$

Merev rotor

Spektroszkópiai termek

$$F(J) = E(J)/hc$$

$$F_{\text{rot}}(J) = \frac{J(J+1)\hbar^2}{2hcMR_e^2} = B_e J(J+1)$$

$$B_e = \frac{\hbar}{4\pi cMR_e^2}$$

A J. és J+1. nívó különbsége

$$\Delta E_{\text{rot}} = E_{\text{rot}}(J+1) - E_{\text{rot}}(J) = \frac{(J+1)\hbar^2}{2MR_e^2}$$

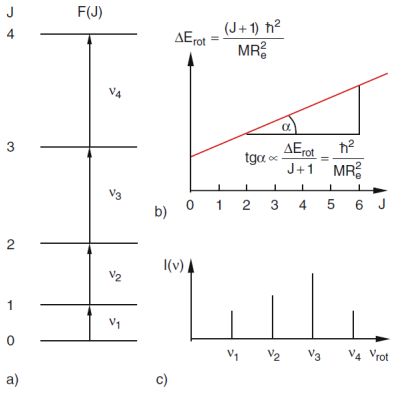


Fig. 9.43. (**a**) Energy levels of the rigid rotor (**b**) Separations $\Delta E_{\text{rot}} = E_{\text{rot}}(J+1) - E_{\text{rot}}(J)$ (**c**) Schematic rotational spectrum

Nagyságrendek

Molecule	R_e/pm	B_e	D_e	α_e	ω_e	$\omega_e x_e$
H_2	74.16	60.8	1.6×10^{-2}	3.06	4401	121.3
Li_2	267.3	0.673	9.9×10^{-6}	0.007	351.4	2.6
N_2	109.4	2.01	5.8×10^{-6}	0.017	2359.0	14.3
O_2	120.7	1.45	4.8×10^{-6}	0.016	1580.0	12.0
I_2	266.6	0.037	4.2×10^{-9}	0.0001	214	0.61
$H^{35}Cl$	127.4	10.59	5.3×10^{-4}	0.31	2990	52.8
$D^{35}Cl$	127.4	5.45	1.4×10^{-4}	0.11	2145	27.2
ICl	232.1	0.114	4.0×10^{-8}	0.0005	384	1.50
CO	112.8	1.931	6×10^{-6}	0.017	2170	13.29
NO	115.1	1.705	0.5×10^{-6}	0.017	1904	14.08

Energia

$$E_{\text{rot}} = (10^{-6}-10^{-2})\, J(J+1)\ \text{eV}$$

Karakterisztikus idő

$$T_{\text{rot}} = \frac{2\pi I/\hbar}{\sqrt{J(J+1)}}$$

$$T_{\text{rot}} = 10^{-14}\ \text{s to}\ 10^{-10}\ \text{s}$$

Átmeneti frekvenciák

$$\nu_{\text{rot}}(J) = [E(J+1)] - E(J)]/\hbar$$

$$\overline{\nu}_{\text{rot}}(J) = 2B_e(J+1) \qquad (\text{cm}^{-1})$$

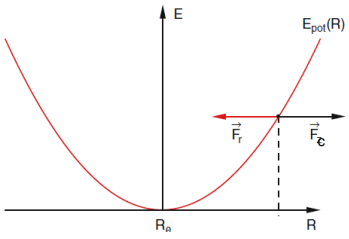
$\nu = 10^9 - 10^{13}$ Hz Gigahertz–Terrahertz

$\lambda = 10^{-5} - 10^{-1}$ m Mikrohullám tartomány

Centrifugális torzulás

- Nem merev molekula
- Forgó rendszer
- Centrifugális erő

$$F_c = -M\omega^2 R$$
$$F_r = -\mathrm{d}E_{pot}(R)/\mathrm{d}R$$



$$\vec{F}_r = -k(R-R_e)\hat{R}$$

Impulzus momentum

$$J^2 = I^2\omega^2 = M^2R^4\omega^2$$

Erőegyensúly

$$M\omega^2 R = \frac{J(J+1)\hbar^2}{MR^3} \stackrel{!}{=} k(R-R_e)$$

$$\Rightarrow R = R_e + \frac{J(J+1)\hbar^2}{MkR^3}, \quad *$$

Rotátor energia

$$E_{rot} = \frac{J(J+1)\hbar^2}{2MR^2} + \frac{1}{2}k(R-R_e)^2$$

$$R = R_e\left(1+\frac{J(J+1)\hbar^2}{MkR_e^4}\right) = R_e(1+x) \qquad x \ll 1$$

$$\frac{1}{R^2} = \frac{1}{R_e^2}\left[1 - \frac{2J(J+1)\hbar^2}{MkR_e^4} + \frac{3J^2(J+1)^2\hbar^4}{M^2kR_e^8} \mp \ldots\right]$$

Sorfejtés és * és $R \approx R_e$

$$E_{rot} = \frac{J(J+1)\hbar^2}{2MR_e^2} - \frac{J^2(J+1)^2\hbar^4}{2M^2kR_e^6} + \frac{3J^3(J+1)^3\hbar^6}{2M^3k^2R_e^{10}} \pm \ldots .$$

Centrifugális torzulás

Termek

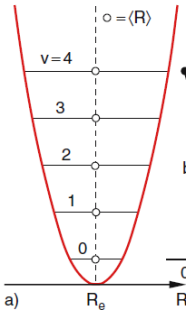
$$F_{rot}(J) = B_eJ(J+1) - D_eJ^2(J+1)^2 + H_eJ^3(J+1)^3 - \ldots$$

$$B_e = \frac{\hbar}{4\pi cMR_e^2}, \quad D_e = \frac{\hbar^3}{4\pi ckM^2R_e^6},$$
$$H_e = \frac{3\hbar^5}{4\pi ck^2M^3R_e^{10}}.$$

Az elektronmozgás hatása……..

Kétatomos molekula rezgései

$$\frac{1}{R^2}\frac{\mathrm{d}}{\mathrm{d}R}\left(R^2\frac{\mathrm{d}S}{\mathrm{d}R}\right) + \frac{2M}{\hbar^2}\left[E - E_{\mathrm{pot}}(R) - \frac{J(J+1)\hbar^2}{2MR^2}\right]S = 0$$



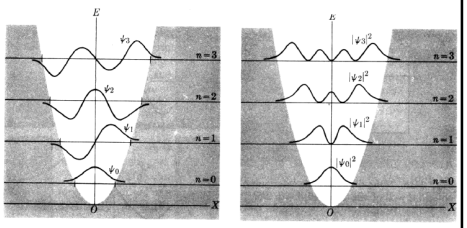
A $S=R\psi_{vib}$ helyettesítéssel harmonikus oszcillátor sajátérték egyenletté alakítható

$$\left(-\frac{\hbar}{2M}\frac{d^2}{dR^2} + E_{pot}\right)\psi_{vib} = E\psi_{vib}$$

$$E_{pot} = \frac{1}{2}k_r(R-R_e) \quad k_r = (\mathrm{d}^2E_{\mathrm{pot}}/\mathrm{d}R^2)_{R_e}$$

$$E(v) = (v+\tfrac{1}{2})h\omega \quad v = 0, 1, 2, \ldots. \quad \omega = \sqrt{k_r/M}$$

$$\psi_{\mathrm{vib}}(R, v) = e^{-\pi M\omega/hR}\cdot H_v(R)$$



Kétatomos molekula rezgései

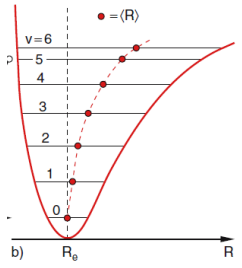
Anharmonicitás

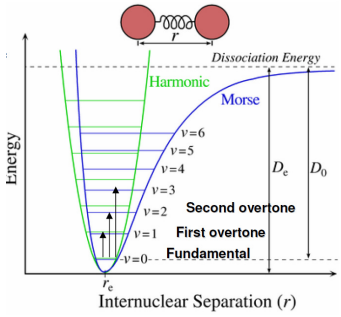
Morse potenciál

$$E_{\mathrm{pot}}(R) = E_{\mathrm{D}}\left[1 - e^{-a(R-R_e)}\right]^2$$

$$E_{\mathrm{vib}}(v) = \hbar\omega_0\left(v+\frac{1}{2}\right) - \frac{\hbar^2\omega_0^2}{4E_{\mathrm{D}}}\left(v+\frac{1}{2}\right)^2$$

$$\Delta E(v) = E_{\mathrm{vib}}(v+1) - E_{\mathrm{vib}}(v) = \hbar\omega\left[1 - \frac{\hbar\omega}{2E_{\mathrm{D}}}(v+1)\right]$$





Rotációs gát, predisszociáció

$$\frac{1}{R^2}\frac{\mathrm{d}}{\mathrm{d}R}\left(R^2\frac{\mathrm{d}S}{\mathrm{d}R}\right) + \frac{2M}{\hbar^2}\left[E - E_{\mathrm{pot}}(R) - \frac{J(J+1)\hbar^2}{2MR^2}\right]S = 0$$

$$E_{\mathrm{pot}}^{\mathrm{eff}}(R) = E_{\mathrm{pot}}^{(v)}(R) + \frac{J(J+1)\hbar^2}{2MR^2}$$

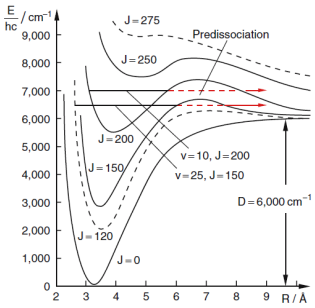


Fig. 9.49. Effective potential curves of the rotating Na_2 molecule for different rotational quantum number J

$$E_{\mathrm{kin}} = E(v, J) - E_{\mathrm{D}}(J = 0)$$

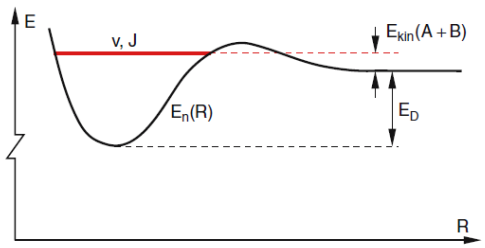


Fig. 9.50. Predissociation of a molecule through the rotational barrier