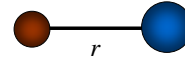


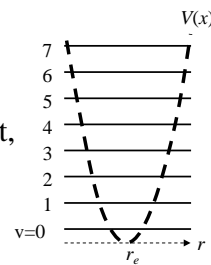
Corrections to Simple Energy Models

- In models we used for diatomic energy modes, we made some simplifying assumptions that are not strictly accurate



1) Non-rigid rotor ($I \neq \text{constant}$)

- as molecule rotates faster, internuclear distance r stretches, **centrifugal distortion**
 - $I \propto r^2$, so $I \uparrow$ and $\epsilon_j \propto 1/I$, so energy level spacing decreases
- vibrating molecule means $r \neq \text{constant}$, **vibration-rotation coupling**
 - not issue for harmonic oscillator, $\langle r^2 \rangle_{\text{avg}} = r_e^2$



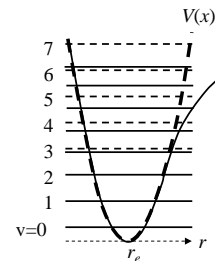
Energy Model Corrections-1
Copyright © 2009 by Jerry M. Seltzman. All rights reserved.

AE/ME 6765

Corrections to Simple Energy Models

2) Anharmonic Oscillator ($k \neq \text{constant}$)

- nonsymmetric potential between nuclei
- repulsion increases rapidly for decreasing r , attraction decreases for larger r
- energy levels get closer together



3) Interaction of Rotations-Electronic (Angular Momentum)

- complex and usually very small change in energies

Energy Model Corrections-2
Copyright © 2009 by Jerry M. Seltzman. All rights reserved.

AE/ME 6765

R-V Energy Corrections

- Rigid rotor model $\epsilon_{rot}(J) = hcBJ(J+1)$
in cm^{-1}
- With corrections *essentially Taylor series expansion in $J(J+1)$*

$$\frac{\epsilon_{rot}(v, J)}{hc} = B_v J(J+1) - \underbrace{D_v [J(J+1)]^2}_{\text{centrifugal distortion in harmonic force field}} + \underbrace{H_v [J(J+1)]^3}_{\text{1st anharmonic term}} + \dots$$

$$B_v = B_e - \alpha_e(v+1/2) + \dots \quad \text{vib. freq. (cm}^{-1}\text{)}$$

$$D_v = D_e + \beta_e(v+1/2) + \dots \quad D_e \cong 4B_e^3/v_e^2$$

$$\Rightarrow D_e \ll B_e$$

$$\Rightarrow D_v \ll B_v$$

values at r_e rot.-vib. coupling

R-V Energy Corrections

- Harmonic oscillator model $\epsilon_{vib}(v) = hc v(v+1/2)$
- With corrections *essentially Taylor series expansion in $(v+1/2)$*

$$\frac{\epsilon_{vib}(v)}{hc} = v_e(v+1/2) - \underbrace{v_e x_e (v+1/2)^2}_{\text{small}} + \underbrace{v_e y_e (v+1/2)^3}_{\text{very small}} + \dots$$

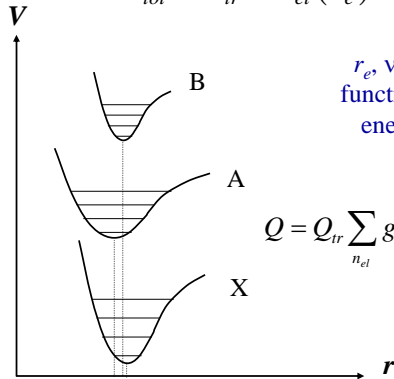
- Generally, molec. constants from spectroscopic data

(cm^{-1})	v_e	$v_e x_e$	B_e	D_e	α_e
H₂	4380	118	60	0.046	3.1
O₂	1580	12	1.5	5×10^{-6}	0.016
NO	1905	14	1.7	5×10^{-6}	0.018

Energy Mode Coupling

- Internal energy modes now coupled

$$\varepsilon_{tot} = \varepsilon_{tr} + \varepsilon_{el}(n_e) + \varepsilon_{vib}(e, v) + \varepsilon_{rot}(e, v, J)$$



r_e, v_e and $v_e x_e$
function of elec.
energy level

B_v, D_v change with
elec. energy level and
vib. energy level

$$Q = Q_{tr} \sum_{n_{el}} g_e e^{-\varepsilon_{el,i}/kT} \sum_v e^{-\varepsilon_{vib}(e,v)/kT} \sum_J (2J+1) e^{-\varepsilon_{rot}(e,v,J)/kT}$$

Energy Model Corrections-5
Copyright © 2009 by Jerry M. Seltzman. All rights reserved.

AE/ME 6765

Corrected Partition Functions

- Can use new expressions to find Q , but in general case they do not reduce to simple analytic expressions

– must use full summations

- For $v_e y_e = \beta_e = H_v = 0$

$$\frac{\varepsilon(v, J)}{hc} = v_e(v+1/2) + B_e J(J+1) - v_e x_e(v+1/2)^2 - D_e [J(J+1)]^2 - \alpha_e(v+1/2)J(J+1)$$

- If corrections small $Q_{rot, vib} \approx Q_{rigid\ rotor} Q_{HO} Q_{corr}$

– with

$$Q_{corr} \cong 1 + 2 \frac{T}{\theta_r} \frac{D_e}{B_e} + \frac{\alpha_e}{B_e} \left(\frac{1}{2} + \frac{1}{e^{\theta_v/T} - 1} \right) + \frac{\theta_{v_x}}{T} \left(\frac{1}{4} + \frac{2}{e^{\theta_v/T} - 1} + \frac{2}{(e^{\theta_v/T} - 1)^2} \right)$$

Energy Model Corrections-6
Copyright © 2009 by Jerry M. Seltzman. All rights reserved.

$$\theta_{v_x} \equiv \frac{hc}{k} v_e x_e \quad \text{AE/ME 6765}$$