CHEMISTRY 163A

EVALUATION OF THE RYDBERG CONSTANT USING THE CORRESPONDENCE PRINCIPLE

The quantum mechanical transition energy, $\tilde{\nu}_{qm}$, must approach the classical value, $\tilde{\nu}_{el}$, in the limit where the transition energies become essentially continuous. Here $n \to \infty$.

$$\tilde{\nu}_{qm} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$\tilde{\nu}_{n \leftarrow n+1} = R\left[\frac{1}{n^2} - \frac{1}{(n+1)^2}\right] \text{ with } n_1 = n,\ n_2 = n + 1$$

$$\tilde{\nu}_{n \leftarrow n+1} = R\frac{(n+1)^2 - n^2}{n^2(n+1)^2} = R\frac{2n+1}{n^2(n+1)^2}$$

$$\lim_{n\to\infty} \tilde{\nu}_{qm} = \frac{2R}{n^3}$$

From Rutherford Atom $\tilde{\nu}_{cl} = \dfrac{\nu_{cl}}{c} = \dfrac{v}{2\pi rc} = \dfrac{1}{2\pi rc}\dfrac{Z^{1/2}e}{(4\pi\varepsilon_0)^{1/2} r^{1/2} m^{1/2}}$

From Bohr-Rydberg: $r = \dfrac{Ze^2}{8\pi\varepsilon_0 Rhc} n^2,\ r^3 = \dfrac{Z^3 e^6 n^6}{512\pi^3 \varepsilon_0{}^3 R^3 h^3 c^3}$

in $\lim_{n \to \infty} \tilde{\nu}_{qm} = \tilde{\nu}_{cl}$

$$\tilde{\nu}_{qm}^2 = \frac{4R^2}{n^6} = \frac{Ze^2}{16\pi^3 \varepsilon_0 m r^3 c^2} = \tilde{\nu}_{cl}^{\,2}$$

$$\frac{4R^2}{n^6} = \frac{Ze^2}{16\pi^3 \varepsilon_0 mc^2} \; \frac{512\pi^3 \varepsilon_0^3 R^3 h^3 c^3}{Z^3 e^6 n^6}$$

$$R_Z = \frac{Z^2 e^4 m}{8\varepsilon_0^2 h^3 c}$$

which is eqn 1-45 in McQ.

$R_{cm^{-1}} = 1.097 \times 10^5\ cm^{-1}$ (Z = 1)

$R_{joules} = hcR_{cm^{-1}} = 2.179914 \times 10^{-18}$ J (Z = 1)

$$r_n = a_0 n^2 \qquad a_0 = \frac{4\pi\hbar^2\varepsilon_0}{Ze^2 m} \qquad \hbar = \frac{h}{2\pi}$$

$a_o = 5.29177 \times 10^{-11}$ m = .529 Å

$$\ell_n = b_o n \qquad b_o = \hbar$$

$b_o = 1.05459 \times 10^{-34}$ J-s

$$E_n = -\frac{Z^2 m e^4}{8\varepsilon_0^2 h^2}\frac{1}{n^2}$$

The general theory of quantum mechanics gives the same relationships for E and ℓ as Bohr atom, but *not* r.