306(4): The H Spectrum from Visible to Far Infra-red

This is given in the following Table:

Transition	Number of Lines	Wavenumber (cm^{-1})
$H\alpha$ $n' = 2$ to $n = 3$	3	15,241.4 (red)
$n' = 3$ to $n = 4$	5	5,334.4 (I.R)
$n' = 4$ to $n = 5$	7	2,469.1 (I.R)
$n' = 5$ to $n = 6$	9	1,338.8 (I.R.)
$n' = 6$ to $n = 7$	11	810.96 (I.R)
$n' = 7$ to $n = 8$	13	524.54 (I.R)
$n' = 8$ to $n = 9$	15	359.94 (F.I.R.)
$n' = 9$ to $n = 10$	17	257.41 (F.I.R.)
$n' = 10$ to $n = 11$	19	190.45 (F.I.R)
$n' = 11$ to $n = 12$	21	144.91 (F.I.R)
$n' = 12$ to $n = 13$	23	102.72 (F.I.R)
$n' = 13$ to $n = 14$	25	81.52 (F.I.R)
$n' = 50$ to $n = 51$	99	1.704 (microwave)

In general there are $2n' - 1$ lines. These are given by using linear polarization ($\Delta m = 0$) and using the Laporte selection rule:

$$\Delta l = 1 \text{ or } -1 \quad -(1)$$

The wavenumber of the transition is given by:

2)

$$\bar{\nu} = 1.097373 \times 10^5 \left(\frac{1}{n'^2} - \frac{1}{n^2} \right) \text{ cm}^{-1}$$

For example:

1) $n' = 2$ to $n = 3$

a) $2s$, $n' = 2$, $l = 0$, $m = 0$
$2p$, $n' = 2$, $l = 1$, $m = -1, 0, 1$

b) $3s$ $n = 3$, $l = 0$, $m = 0$
$3p$ $n = 3$, $l = 1$, $m = -1, 0, 1$
$3d$ $n = 3$, $l = 2$, $m = -2, -1, 0, 1, 2$

There are three transitions for $\Delta m = 0$:

$$2s \rightarrow 3p \quad (\Delta l = 1)$$
$$\left\{ \begin{array}{l} 2p \rightarrow 3s \quad (\Delta l = -1) \\ 2p \rightarrow 3d \quad (\Delta l = 1) \end{array} \right.$$

In the absence of any external influence, and in the absence of Evans / Morris shifts, these are degenerate, so all occur at the same frequency, 15,241.4 cm^{-1} in the red part of the visible. According to basic quantum theory these are split into three different lines by the Evans / Morris shifts. (UFT304).

2) $n' = 3$ to $n = 4$

As in the previous note there are five transitions:

$$3s \rightarrow 4p \quad (\Delta l = 1)$$
$$\left\{ \begin{array}{l} 3p \rightarrow 4s \quad (\Delta l = -1) \\ 3p \rightarrow 4d \quad (\Delta l = 1) \end{array} \right.$$
$$\left\{ \begin{array}{l} 3d \rightarrow 4p \quad (\Delta l = -1) \\ 3d \rightarrow 4f \quad (\Delta l = 1) \end{array} \right.$$

3) It can be seen that the transitions occur in pairs except for the stop transition.

3) For $n' = 4$ to $n = 5$
there are seven transitions:

$$4s \rightarrow 5p \quad (\Delta l = 1)$$
$$4p \rightarrow 5s \quad (\Delta l = -1)$$
$$4p \rightarrow 5d \quad (\Delta l = 1)$$
$$4d \rightarrow 5p \quad (\Delta l = -1)$$
$$4d \rightarrow 5f \quad (\Delta l = 1)$$
$$4f \rightarrow 5d \quad (\Delta l = -1)$$
$$4f \rightarrow 5e \quad (\Delta l = 1)$$

According to basic quantum theory there are split into seven different lines by the Evans Morris effects.
In general there are $2n' - 1$ lines. As the table shows they cover the range from the red to the far infra-red at 81.52 cm^{-1} for $n' = 13$.
For the $n' = 50$ to the $n = 51$ transition there are 99 lines, and the transition occurs at

$$1.704 \text{ cm}^{-1} = 51.12 \text{ GHz} \qquad -(2)$$

in the microwave. Therefore 99 red shifted lines should be observable.

All these results come from the Beer

4) Lambert law:

$$\frac{I}{I_0} = \exp(-\alpha Z) \quad -(3)$$

where I_0 is the initial intensity of the radiation, I its intensity after traversing a distance Z through an absorber, and α the power absorption coefficient. As in eq. (13) of UFT300, the intensity in the Planck distribution is:

$$I = \frac{\hbar\omega^3}{\pi^2 c^2}\left(\exp\left(\frac{\hbar\omega}{kT}\right) - 1\right)^{-1} \quad -(4)$$

in joules per square metre.

This is a foundational result of the quantum theory.

It follows that:

$$I_0 = \frac{\hbar\omega_0^3}{\pi^2 c^2}\left(\exp\left(\frac{\hbar\omega_0}{kT}\right) - 1\right)^{-1} \quad -(5)$$

So:

$$\frac{I}{I_0} = \left(\frac{\omega}{\omega_0}\right)^3 \left(\frac{e^{y_0} - 1}{e^{y} - 1}\right) \quad -(6)$$

where:

6)

$$y_0 = \frac{\hbar\omega_0}{kT}, \quad y = \frac{\hbar\omega}{kT} \quad -(7)$$

The power absorption coefficient can be integrated across an absorption line to give:

$$A = \left(\frac{N}{V}\right) \frac{|\mu_{fi}|^2}{6\epsilon_0 v\hbar} \quad -(8)$$

Eq. (8) is again the result of foundational quantum theory. Here there are N molecules in a sample volume V, μ_{fi} is the transition electric dipole moment, v the velocity of the probe radiation in the sample, ϵ_0 the vacuum S.I. permittivity and $\hbar$ the reduced Planck constant. In dilute gaseous hydrogen:

$$v \sim c. \quad -(9)$$

Therefore, according to foundational quantum theory:

$$\boxed{\left(\frac{\omega}{\omega_0}\right)^3 \left(\frac{e^{y_0} - 1}{e^{y} - 1}\right) = \exp\left(-\left(\frac{N}{V}\right) \frac{|\mu_{fi}|^2}{6\epsilon_0 v\hbar} Z\right)} \quad -(9)$$

As shown in the Table the atomic H spectrum covers the visible to microwave range, and beyond to radio frequencies.

7) Approximations of Eq. (9)

1) If $\hbar\omega \gg kT$; $\hbar\omega_0 \gg kT$ – (10)

then:

$$\frac{\omega}{\omega_0} = \exp\left(-\frac{AZ}{3}\right) \quad -(11)$$

2) If $\hbar\omega \ll kT$; $\hbar\omega_0 \ll kT$ – (12)

then

$$\frac{\omega}{\omega_0} = \exp\left(-\frac{AZ}{2}\right) \quad -(13)$$

These are the Evans / Morris shifts, predicted by fundamental quantum theory.

As in note 304(3) the transition dipole moment is calculated from:

$$\langle\mu\rangle_{12} = \int \phi_1^* er\cos\theta\, \phi_2 \, d\tau \quad -(14)$$

in linear polarization, where:

$$\Delta m = 0 \quad -(15)$$

So:

$$\langle\mu_{12}\rangle = \int_{\phi=0}^{2\pi}\int_{\theta=0}^{\pi}\int_{r=0}^{\infty} \phi_1^* er\cos\theta\, \phi_2\, r^2 \sin\theta \, dr\, d\theta\, d\phi \quad -(16)$$

The transition dipole moment is different for

8) each different transition from ϕ_1 to ϕ_2.

for example, for the 2s to 3p transition:

$$\langle \mu(2s \to 3p) \rangle = \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} \int_{r=0}^{\infty} \phi^*(2s)\, e r^3 \cos\theta \sin\theta\, \phi(3p)\, dr\, d\theta\, d\phi \quad -(17)$$

So for the αH line of the Balmer series there are three different Evans / Morris shifts:

1) $\omega(2s \to 3p) = \omega_0 \exp\left(-\frac{A(2s \to 3p) Z}{3}\right)$

2) $\omega(2p \to 3s) = \omega_0 \exp\left(-\frac{A(2p \to 3s) Z}{3}\right)$

3) $\omega(2p \to 3d) = \omega_0 \exp\left(-\frac{A(2p \to 3d) Z}{3}\right)$.

Similarly for the far infra-red line at $81.52\ cm^{-1}$ ($n' = 13$ to $n = 14$) there are twenty five different Evans / Morris shifts.

For the microwave line at $1.704\ cm^{-1}$ or 51.12 GHz there are ninety nine different Evans / Morris shifts.

The extent of all these shifts depends on the sample path length Z.