

The following table of hydrogen transition data is from “Atomic Transition Probabilities,” 1966.

| Transition | $\lambda(\text{\AA})$ | $E_i(\text{cm}^{-1})$ | $E_k(\text{cm}^{-1})$ | g_i | g_k | $A_{ki}(\text{sec}^{-1})$ | f_{ik} |
|------------|-----------------------|-----------------------|-----------------------|-------|-------|---------------------------|------------------------|
| $1s-2p$ | 1215.67 | 0 | 82259 | 2 | 6 | 6.265×10^8 | 0.4162 |
| $1s-3p$ | 1025.72 | 0 | 97492 | 2 | 6 | 1.672×10^8 | 7.910×10^{-2} |
| $1s-4p$ | 972.537 | 0 | 102824 | 2 | 6 | 6.818×10^7 | 2.899×10^{-2} |
| $1s-5p$ | 949.743 | 0 | 105292 | 2 | 6 | 3.437×10^7 | 1.394×10^{-2} |
| $1s-6p$ | 937.804 | 0 | 106632 | 2 | 6 | 1.973×10^7 | 7.800×10^{-3} |
| $2p-3s$ | 6562.86 | 82259 | 97492 | 6 | 2 | 6.313×10^6 | 1.359×10^{-2} |
| $2p-4s$ | 4861.35 | 82259 | 102824 | 6 | 2 | 2.578×10^6 | 3.045×10^{-3} |
| $2p-5s$ | 4340.48 | 82259 | 105292 | 6 | 2 | 1.289×10^6 | 1.213×10^{-3} |
| $2p-6s$ | 4101.75 | 82259 | 106632 | 6 | 2 | 7.350×10^5 | 6.180×10^{-4} |
| $2s-3p$ | 6562.74 | 82259 | 97492 | 2 | 6 | 2.245×10^7 | 0.4349 |
| $2s-4p$ | 4861.29 | 82259 | 102824 | 2 | 6 | 9.668×10^6 | 0.1028 |
| $2s-5p$ | 4340.44 | 82259 | 105292 | 2 | 6 | 4.948×10^6 | 4.193×10^{-2} |
| $2s-6p$ | 4101.71 | 82259 | 106632 | 2 | 6 | 2.858×10^6 | 2.163×10^{-2} |
| $2p-3d$ | 6562.81 | 82259 | 97492 | 6 | 10 | 6.465×10^7 | 0.6958 |
| $2p-4d$ | 4861.33 | 82259 | 102824 | 6 | 10 | 2.062×10^7 | 0.1218 |
| $2p-5d$ | 4340.47 | 82259 | 105292 | 6 | 10 | 9.425×10^6 | 4.437×10^{-2} |
| $2p-6d$ | 4101.74 | 82259 | 106632 | 6 | 10 | 5.145×10^6 | 2.163×10^{-2} |

The $3 \rightarrow 2$ transitions emit the bright red H- α line.

| Transition | $\lambda (\text{\AA})$ | $A_{ki} (\text{second}^{-1})$ |
|------------|------------------------|-------------------------------|
| $2p-3s$ | 6562.86 | 6.313×10^6 |
| $2s-3p$ | 6562.74 | 2.245×10^7 |
| $2p-3d$ | 6562.81 | 6.465×10^7 |

Let us compute the spontaneous emission coefficients A_{ki} for H- α and see if the results match the table.

The orbital names correspond to the following angular momenta.

| Letter | Angular momentum ℓ |
|--------|-------------------------|
| s | 0 |
| p | 1 |
| d | 2 |

Because of the magnetic quantum number m_ℓ there are multiple processes for each transition.

There are three processes for the transition $3s \rightarrow 2p$.

$$\begin{aligned}\psi_{3,0,0} &\rightarrow \psi_{2,1,1} \\ \psi_{3,0,0} &\rightarrow \psi_{2,1,0} \\ \psi_{3,0,0} &\rightarrow \psi_{2,1,-1}\end{aligned}$$

There are three processes for the transition $3p \rightarrow 2s$.

$$\begin{aligned}\psi_{3,1,1} &\rightarrow \psi_{2,0,0} \\ \psi_{3,1,0} &\rightarrow \psi_{2,0,0} \\ \psi_{3,1,-1} &\rightarrow \psi_{2,0,0}\end{aligned}$$

Finally, there are fifteen processes for the transition $3d \rightarrow 2p$.

$$\begin{array}{lll}
\psi_{3,2,2} \rightarrow \psi_{2,1,1} & \psi_{3,2,2} \rightarrow \psi_{2,1,0} & \psi_{3,2,2} \rightarrow \psi_{2,1,-1} \\
\psi_{3,2,1} \rightarrow \psi_{2,1,1} & \psi_{3,2,1} \rightarrow \psi_{2,1,0} & \psi_{3,2,1} \rightarrow \psi_{2,1,-1} \\
\psi_{3,2,0} \rightarrow \psi_{2,1,1} & \psi_{3,2,0} \rightarrow \psi_{2,1,0} & \psi_{3,2,0} \rightarrow \psi_{2,1,-1} \\
\psi_{3,2,-1} \rightarrow \psi_{2,1,1} & \psi_{3,2,-1} \rightarrow \psi_{2,1,0} & \psi_{3,2,-1} \rightarrow \psi_{2,1,-1} \\
\psi_{3,2,-2} \rightarrow \psi_{2,1,1} & \psi_{3,2,-2} \rightarrow \psi_{2,1,0} & \psi_{3,2,-2} \rightarrow \psi_{2,1,-1}
\end{array}$$

For each process, A_{ki} can be computed using the following Heisenberg formula.

$$A_{ki} = \frac{e^2}{3\pi\epsilon_0\hbar c^3} \omega_{ki}^3 |r_{ki}|^2$$

The transition frequency ω_{ki} is given by Bohr's frequency condition.

$$\omega_{ki} = \frac{1}{\hbar}(E_k - E_i)$$

The transition probability (multiplied by a physical constant) is

$$|r_{ki}|^2 = |x_{ki}|^2 + |y_{ki}|^2 + |z_{ki}|^2$$

For wave functions ψ in spherical coordinates we have the following transition amplitudes.

$$\begin{aligned}
x_{ki} &= \int \psi_k^*(r \sin \theta \cos \phi) \psi_i dV \\
y_{ki} &= \int \psi_k^*(r \sin \theta \sin \phi) \psi_i dV \\
z_{ki} &= \int \psi_k^*(r \cos \theta) \psi_i dV
\end{aligned}$$

The average A_{ki} is obtained by summing over m_ℓ states and dividing by the number of distinct initial states.

Using Eigenmath we obtain

$$\begin{aligned}
A_{3s2p} &= 6.31358 \times 10^6 \text{ second}^{-1} \\
A_{3p2s} &= 2.24483 \times 10^7 \text{ second}^{-1} \\
A_{3d2p} &= 6.4651 \times 10^7 \text{ second}^{-1}
\end{aligned}$$

which is very close to the values shown in the table.