

1. HÖNL-LONDON FACTORS

Electric dipole transitions in diatomic molecules from a given electronic and vibrational term n to another given electronic and vibrational term n' are accompanied in general by a change in the orbital angular momentum of the nuclei. To the extent that the total wavefunction is a product of nuclear and electronic parts, the probability for a transition can be factored into a part which depends on the quantum numbers for the nuclear angular momentum, and a part which is independent of the nuclear angular momentum. The factor which gives the dependence on the nuclear angular momentum is called the **Hönl-London** factor.

1.1. Zero electron spin.

Consider first the case where there the spin of the electrons is zero. As usual, let \mathbf{K} denote the total orbital angular momentum, which is the sum of the electronic and nuclear orbital angular momenta (without any spin)

$$\mathbf{K} \equiv \mathbf{L}_{\text{elec}} + \mathbf{L}_{\text{nuc}} . \quad (1.1)$$

Since the component of the nuclear angular momentum along the nuclear axis ζ vanishes, the component K_ζ of \mathbf{K} along the molecular axis is just the electronic component

$$K_\zeta = \Lambda . \quad (1.2)$$

Let \mathbf{d} be the electric dipole operator, which is a sum of electronic and nuclear parts

$$\mathbf{d} \equiv \mathbf{d}_{\text{elec}} + \mathbf{d}_{\text{nuc}} . \quad (1.3)$$

The probability for an electric dipole transition

$$n'K'\Lambda' \rightarrow nK\Lambda \quad (1.4)$$

is then proportional to the square of the dipole matrix element

$$|\langle n'K'\Lambda' | \mathbf{d} | nK\Lambda \rangle|^2 = f(K', \Lambda' | K, \Lambda) |\langle n'\Lambda' | \mathbf{d} | n\Lambda \rangle|^2 . \quad (1.5)$$

The quantity $f(K', \Lambda' | K, \Lambda)$ in equation (1.5) is the Hönl-London factor, and it contains all the dependence of the transition probability on the nuclear angular momentum. The Hönl-London factors are symmetric in $(K', \Lambda') \rightarrow (K, \Lambda)$

$$f(K', \Lambda' | K, \Lambda) = f(K, \Lambda | K', \Lambda') . \quad (1.6)$$

The quantity $|\langle n'\Lambda' | \mathbf{d} | n\Lambda \rangle|^2$ in equation (1.5) is the square of the matrix element of the dipole operator \mathbf{d} evaluated in a frame of reference in which the molecule is taken to be non-rotating, and the z -axis is taken to lie along the axis ζ of the molecule.

The dipole moment of a molecule in its ground electronic and vibrational state $n_0\Lambda_0$ is called its **permanent dipole moment**,

$$\langle n_0\Lambda_0 | \mathbf{d} | n_0\Lambda_0 \rangle = \mathbf{d}_{\text{permanent}} , \quad (1.7)$$

which is aligned with the molecular axis.

It should be noted that the Hönl-London factors are defined with the statistical weight factors $2K_L + 1$ and $2K_U + 1$ included; that is, the probabilities as given are summed over lower and upper rotational states. If, as is true in thermodynamic equilibrium, and is often true in practice, the upper rotational levels are all equally occupied, then the Hönl-London factor correctly gives the transition probability out of all the upper rotational states. But the transition probability for emission out of an individual upper state is the Hönl-London factor divided by the statistical weight factor $2K_U + 1$ of the upper level. Similarly, the transition probability for absorption from an individual lower state is the Hönl-London factor divided by the statistical weight factor $2K_L + 1$ of the lower level.

The Hönl-London factors for the Q -branch ($K' = K$) are:

$$f(K, \Lambda|K, \Lambda) = \frac{\Lambda^2(2K + 1)}{K(K + 1)}, \quad (1.8a)$$

$$f(K, \Lambda + 1|K, \Lambda) = \frac{(K - \Lambda)(K + \Lambda + 1)(2K + 1)}{4K(K + 1)}. \quad (1.8b)$$

The Hönl-London factors for the P and R -branches ($K' = K \pm 1$) are:

$$f(K + 1, \Lambda|K, \Lambda) = \frac{(K - \Lambda + 1)(K + \Lambda + 1)}{K + 1}, \quad (1.9a)$$

$$f(K + 1, \Lambda + 1|K, \Lambda) = \frac{(K + \Lambda + 1)(K + \Lambda + 2)}{4(K + 1)}, \quad (1.9b)$$

$$f(K + 1, \Lambda - 1|K, \Lambda) = \frac{(K - \Lambda + 1)(K - \Lambda + 2)}{4(K + 1)}. \quad (1.9c)$$

1.2. Hund case (a).

The Hönl-London factors are as above, with (J, Ω) in place of (K, Λ) . Equation (1.5) is replaced by

$$|\langle n' J' \Omega' | \mathbf{d} | n J \Omega \rangle|^2 = f(J', \Omega' | J, \Omega) |\langle n' \Omega' \Lambda' | \mathbf{d} | n \Omega \Lambda \rangle|^2. \quad (1.10)$$

Since spin does not change in an electric dipole transition, the change in $\Omega \equiv \Lambda + \Sigma$ is equal to the change in Λ , that is, $\Omega' - \Omega = \Lambda' - \Lambda$.

1.3. Hund case (b).

Hönl-London factors

$$f(J', K', S, \Lambda' | J, K, S, \Lambda) \quad (1.11)$$

exist also in this case, but the formulae are more complicated.

If the fine-structure levels J in a given K are populated in thermodynamic equilibrium (in effect, in proportion to the statistical weights $2J + 1$), then the transition probabilities from level K to K' are given by the Hönl-London factors above.