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transition (dipole) moment

Also contains definition of: electronic transition moment

An electromagnetic wave may induce an oscillating electric moment in a molecule (possibly leading to absorption if the oscillation frequency is equal to the light frequency). The amplitude of this moment is the transition momentbetween the initial (i) and final (f) states (here assumed to be non-degenerate):

$$\boldsymbol{M}_{\mathrm{if}} = \langle \mathrm{f} \mid \boldsymbol{M}_{\mathrm{op}} \mid \mathrm{i} \rangle$$

where $\boldsymbol{M}_{\mathrm{op}}$ is the electric dipole moment operator, a vector operator that is the sum of the position vectors of all charged particles weighted with their charge. The transition moment $\boldsymbol{M}_{\mathrm{if}}$ is a vector in the molecular framework, characterized both by its direction and its probability.

Notes:

1. The absorption probability for linearly polarized light is proportional to the cosine square of the angle between the electric vector of the electromagnetic wave and $\boldsymbol{M}_{\mathrm{if}}$; light absorption will be maximized if they are parallel, and no absorption will occur if they are perpendicular.
2. It is frequently said that a transition is polarized along the direction of its transition moment and this direction is called the polarization direction of the transition.
3. In the case of a doubly degenerate final state f, each of the two components at the same energy has a transition moment and the two moments define a plane. The transition is then said to be polarized in that plane, which also defines its polarization direction(s). This is typically the case for some of the transitions in highly symmetrical molecules.
4. In the case of a vibronic transition, where both the initial and the final states may be characterized by (different) electronic and vibrational states, the Franck–Condon principle is often applied. This approximation separates electronic and nuclear descriptions and allows the transition moment to be written as a product of a purely electronic transition moment and an overlap integral between the two vibrational wavefunctions involved.

Source:

PAC, 2007, *79*, 293 *(Glossary of terms used in photochemistry, 3rd edition (IUPAC Recommendations 2006))* on page 434

