SEMESTER VI

(PHYSICAL CHEMISTRY HONOURS)

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SPECTROSCOPY :

LINE WIDTH AND INTENSITY OF SPECTRAL LINES

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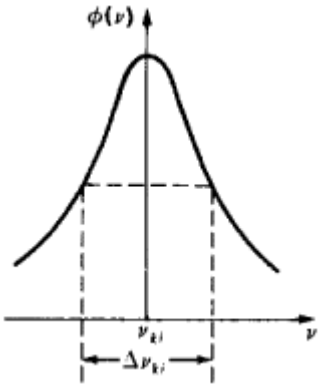
Q. What are the factors governing width of spectral lines



Broadening is the "natural line width" which arises from

- Uncertainty Principle : uncertainty in energy of the states involved in the transition
-
  - Physical mechanisms can broaden spectral lines.
    - Doppler Effect
      - Thermal motion
      - Rotation
      - Gas Turbulence
    - Collision Broadening
    - Magnetism
- In quantum mechanics, electrons can jump from one state to another with radiation absorption/emission. However, the frequency of the radiation doesn't have to be exactly $\frac{E_2-E_1}{h}$. One can use a slightly different frequency and still get the energy transition. This means that if you look at the spectrum of light emitted/absorbed from an atom, you son't see a sharp delta function, but a smooth curve (line) that looks like a Lorentzian. **This means the absorption line is broader than the case of just a single frequency getting absorbed**. This is where the term "**line broadening**" comes from - it is the phenomenon of an absorption curve getting broader (meaning more and more frequencies are able to get absorbed by an electron or emitted by one). There are a couple of reasons for the absorption line to get broader, such as pressure, Doppler effect, and more - but as said earlier, even a single atom in vacuum has a "natural broadening".

This is due to the finite time an electron spends (on average) in the excited state. This transition is because that the hamiltonian of an atom in a vacuum is perturbed by the electromagnetic field in the vacuum. In perturbation theory, one can see that the more time it takes for a perturbation to induce a transition, the more precise its frequency needs to be, meaning

Detailed algebra involving the time-dependent perturbation theory allows us to derive a theoretical expression for the Einstein coefficient of induced absorption

$$B_{ij} = \frac{\left|\vec{M}_{ij}\right|^2}{6\varepsilon_0 h^2} = \frac{8\pi^3}{3h^2(4\pi\varepsilon_0)}\left|\vec{M}_{ij}\right|^2$$

where the radiation density is expressed in units of Hz.

By definition, the dipole moments of two given states *i* and *j* are

$$\left|\vec{M}_{ii}\right| = \int_{-\infty}^{+\infty} \psi_i^* \hat{\mu} \psi_i \, d\tau$$

The quantity $|M_{ij}|$ is known as the ***transition moment integral***, having the same unit as dipole moment, i.e. C m. Apparently, if this quantity is zero for a particular transition, the transition probability will be zero, or, in other words, the transition is forbidden. This forms the basis for the selection rules for transitions.

Intensity of spectral lines

- The transition probability between the two states (selection rules)

Transition dipole moment

$$\mu_{fi} = \int \Psi_f \hat{\mu} \Psi_i \, d\tau = \left\langle \Psi_f \left| \hat{\mu} \right| \Psi_i \right\rangle$$

Only if this integral is non-zero, the transition is allowed

Selection rules tell us the possible transitions among quantum levels due to absorption or emission of electromagnetic radiation. Incident electromagnetic radiation presents an oscillating electric field $E_0\cos(\omega t)$ that interacts with a transition dipole. The dipole moment vector is $\boldsymbol{\mu} = e\mathbf{r}$, where $\mathbf{r}$ is a vector pointing in a direction of space.

By definition, the dipole moments of two given states *i* and *j* are

$$\left|\vec{M}_{ii}\right| = \int_{-\infty}^{+\infty} \psi_i^* \hat{\mu} \psi_i \, d\tau$$

$$\left|\vec{M}_{jj}\right| = \int_{-\infty}^{+\infty} \psi_j^* \hat{\mu} \psi_j \, d\tau$$

respectively.

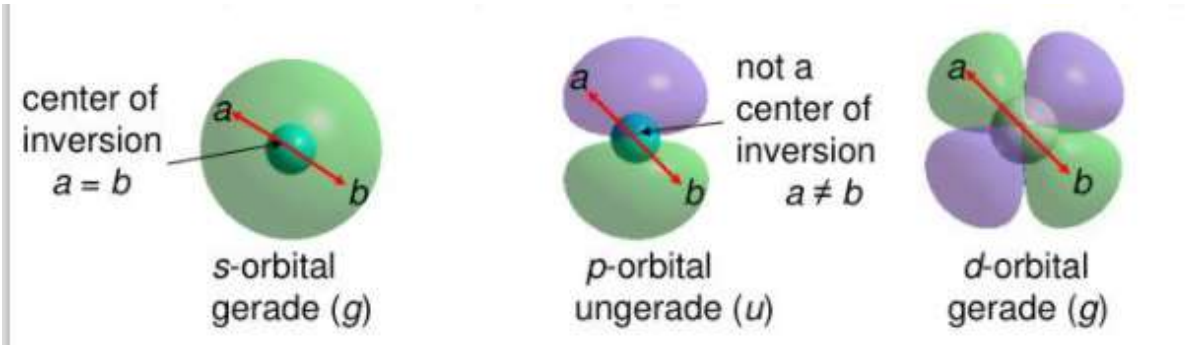
The symbol $\left|\vec{M}_{ij}\right| = \int_{-\infty}^{+\infty} \psi_j^* \hat{\mu} \psi_i \, d\tau$ signifies the transition dipole moment for a transition from the *i* state to the *j* state, and signifies a transient dipolar polarization created by an interaction of electromagnetic radiation with a molecule.

Overview of Selection Rules

|**Mij**| is a triple integral involving the complex conjugate of the excited state wave function, the dipole moment operator and the wave function of the ground state. Though the quantum mechanical solution of wave functions for the ground and excited states is complicated, it is often possible to deduce the selection rules from the symmetry properties of the wave functions alone.

Wave functions that do not change sign on reflection (r → -r) are said to be of even parity and those that change sign are of odd parity. The dipole moment operator transforms as r, since for a single electron, the **dipole moment** operator is **er**, where e is the electronic charge. Thus it is of **odd parity**. For the transition moment integral to survive, therefore, the product of the two wave functions should also be of odd parity, since odd × odd = even. This is only possible if one is odd and the other even, since odd × even = odd. We immediately have the **Laporte selection rule**, which states that the wave function should change its parity during a transition.

This rule is also stated as follows: g ↔ u, but g ↮ g and u ↮ u. This notation originates from the German gerade for wave functions of even parity, denoted as g, and ungerade for wave function of odd parity (denoted by u), in the case of **centrosymmetric molecules**.



It is apparent that the s and d orbitals are of even parity and hence transitions cannot take place between them. However,

the p orbitals are of odd parity and hence transitions between the s and p orbitals may be possible. Though these are allowed transitions by electric dipole selection rules, the argument does not explain why s to f transitions are forbidden, though these transitions involve a change of parity. It is important to remember that the symmetry selection rules only tell us which transitions are forbidden by symmetry, but it does not follow that the remaining transitions are allowed. They may be forbidden for reasons other than symmetry. In the present case, **conservation of angular momentum requires that the angular momenta of the atom and photon should remain constant**. **Since the photon has an intrinsic angular momentum of one, it can either add one unit or subtract one unit of angular momentum from the atom.** In other words, the l quantum number can either decrease or increase by one unit, or $\mathbf{\Delta l = \pm 1}$. Hence, an s electron can only be promoted to a p orbital.

- $\mathbf{\Delta l = \pm 1}$

Every kind of spectroscopy has two parts to the selection rules: a ***gross selection rule*** and a ***specific selection rule***. The gross selection rule states the requirements for an atom or molecule to display a particular spectrum and the specific selection rule states the changes in quantum numbers accompanying the transitions. The gross selection rule is often easy to predict based on the requirements for effective interaction with the electromagnetic field.

To summarize:

Selection Rules of electronic transition

- Electronic transitions may be classed as intense or weak according to the magnitude of ε_{max} that corresponds to *allowed* or *forbidden* transition as governed by the following **selection rules** of electronic transition:
- 1. **Spin selection rule**: there should be no change in spin orientation or no spin inversion during these transitions. Thus, S→S, T→T, are allowed, but S→T, T→S, are forbidden.

Selection Rules of electronic transition

- 2. **Angular momentum rule**: the change in angular momentum should be within one unit (0 or ±1).
- 3. **Symmetry rule**: the product of the electric dipole vector and the group theoretical representations of the two states is totally symmetric.
- The spin selection rule simply states that transitions between states of different multiplicities are forbidden.