Molecular Spectra

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Molecular spectra

Molecules typically rotate and vibrate simultaneously. Motions are approx. independent, so the total E is given by

$$E_{\text{rot-vib}} = \frac{\hbar^2}{2I_{CM}}\ell(\ell+1) + (\nu + \frac{1}{2})\hbar\omega$$

This gives simplest approx to *rotation-vibration spectrum*

- Vibration levels more widely spaced—leads to levels “split” by rotational levels.

- Temperature or EM radiation can cause transitions

- Energy, angular momentum, etc. must be conserved

- Transitions involving electromagnetic radiation—*optical transitions.*

Transition rules To satisfy conservation laws, place restrictions on quantum numbers allowed* in transition.

Any optical transition between levels with energy E_1 and E_2 gives photon emission or absorption at

$$f = \frac{|E_2 - E_1|}{h} \text{ or } \Delta E = \pm hf$$

This is conservation of energy for molecule and photon. There must be a *resonance* between E level and photon. If not photons of proper E available, no transition.

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* "Forbidden" transitions *do* occur—but with much lower probability.

Initial and final states for an optical transition must differ by

$$|\ell_2 - \ell_1| = 1 \text{ or } \Delta\ell = \pm 1$$

This means the photon carries away angular momentum of $\hbar$, so a photon is a spin-1 particle. This is then an expression of conservation of angular momentum for photon and molecule.

The previous two equations are the *selection rules for optical transitions.*

Lower vibrational level transitions have the restriction

$$|\nu_2 - \nu_1| = 1 \text{ or } \Delta\nu = \pm 1$$

This is due to harmonic character of interatomic force (and potential.) Since for large displacements, the potential is not harmonic, for high E vibration levels this is not valid.

All relevant selection rules must be obeyed simultaneously. So pure rotational ($\Delta\nu = 0$) and pure vibrational ($\Delta\ell = 0$) transitions are forbidden—optical transitions usually involve both vibration and rotation.

Example—molecular absorption spectrum

At typical T, only the $\nu = 0$ states will be excited. So if a photon is absorbed, it must be that

$$\nu \to \nu + 1 \text{ and } \ell \to \ell \pm 1$$

in other words,

$$\Delta\nu = +1 \text{ and } \Delta\ell = \pm 1.$$

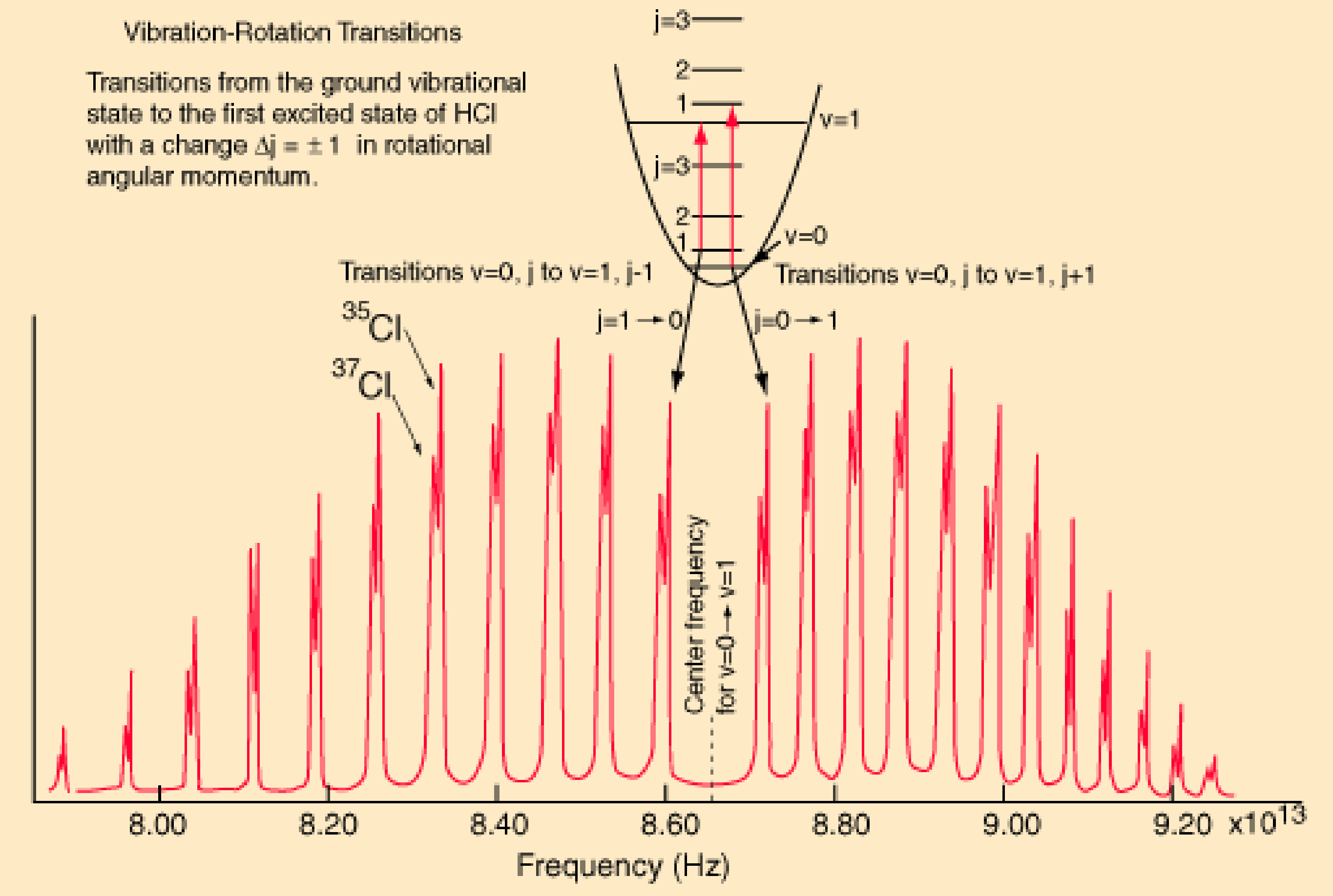
This gives absorbed photon energies

$$\begin{aligned} \Delta E &= \hbar\omega + \frac{\hbar^2}{I_{CM}}(\ell+1) \;\; \text{for } \ell = 0, 1, \ldots \; (\Delta\ell = +1), \\ \Delta E &= \hbar\omega - \frac{\hbar^2}{I_{CM}}\ell \;\; \text{for } \ell = 1, 2, \ldots \; (\Delta\ell = -1). \end{aligned}$$

Predicted and experimental forms for this type of spectrum for a diatomic molecule are shown by figs. 11.11 and 11.12.

In the actual HCl spectrum, the lines are not equal strengths because these depend on transitions *rates*, which depend on the populations of the state, which depend on T and degeneracies of the states.

Here is an HCl spectrum



Vibration-Rotation Transitions

Transitions from the ground vibrational state to the first excited state of HCl with a change Δj = ± 1 in rotational angular momentum.

j = ℓ in our notation.

From `http://hyperphysics.phy-astr.gsu.edu/hbase/molecule/vibrot.html#c1`

Atmospheric models

The vibration-rotation spectrum of gases is extremely important in the radiative balance of energy in the Earth's atmosphere.

IR absorption by H_2O, CO_2 and CH_4 is responsible for most of the greenhouse effect.

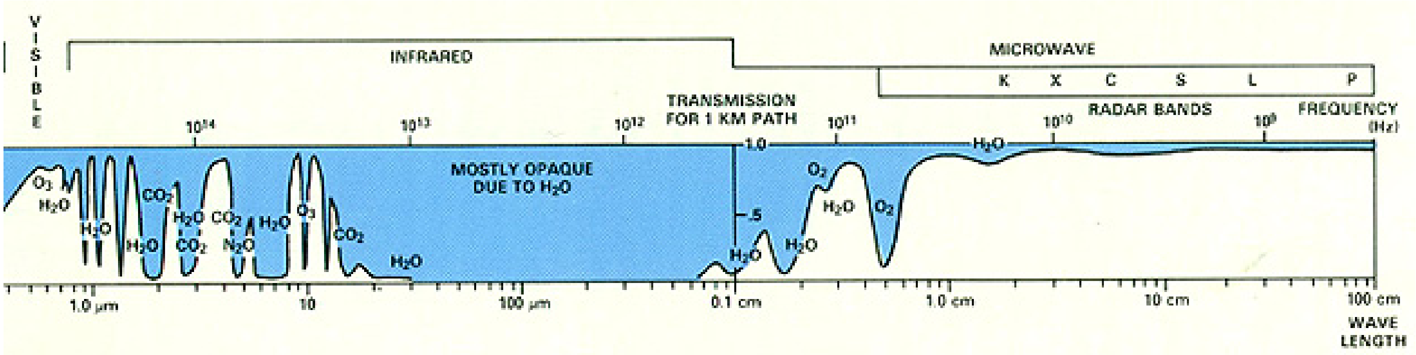
There is an excellent online atmospheric model at:

`http://geosci.uchicago.edu/`
`~archer/cgimodels/radiation.html`

which is explained in an exercise using it at:

`http://geosci.uchicago.edu/`
`~archer/PS134/LabManual/lab.modtran.html`

Here is a generic plot of atmospheric transmission from the IR through microwaves:



From `http://rst.gsfc.nasa.gov/Intro/Part2_4.html`

Scattering

Molecules may *scatter* radiation, with no resonance involved.

Rayleigh scattering —photon E is unchanged by collision. More intense for shorter wavelengths:

$$I_{\text{scat}} \propto 1/\lambda^4.$$

This is responsible for blue of the sky, as blue light is shorter λ.

Raman scattering occurs with photon changing E in interaction with molecule. Rotation is involved with selection rule $\Delta\ell = \pm 2$.

Raman shift

Photon interacts with molecule, and has initial E and final E'. The rotation quantum number of the molecule changes by $\ell \to \ell + 2$, so the scattered photon loses energy and has a frequency shift of

$$f - f' = \frac{\hbar}{2\pi I_{CM}}(2\ell + 3)$$

This can be used to measure I_{CM} for the molecule. Raman scattering is weak, but modern laser sources also make it useful for detection of trace molecules.

Electronic-vibration spectra

The same “level-splitting” process can happen with combined electronic and vibration state transitions of a molecule, like the combined rotation-vibration schemes we have just seen.

For each electronic state, there is associated a set of vibration states, etc.

These transitions lie mostly in visible and UV range.

Fluorescence and phosphorescence

Follow the same basic pattern:

1. Molecule absorbs photon → excited electronic-vibration state.
2. Molecule loses some E in collisions with neighbors.
3. Molecule emits a photon with lower E than original—*Stokes shift.*

For typical fluorescent paint, UV photon absorbed, visible photon emitted.

In phosphorescence, step 2 is to a metastable state, so step 3 requires a “forbidden” transition that takes a long time. “Glow-in-the dark” items.