
PHY2505S

Atmospheric Radiative Transfer and Remote Sounding

Lecture 9

- Vibration-Rotation Spectra
- Band Nomenclature
- Width and Shape of Spectral Lines

Vibration-Rotation Spectra

From Lecture 8:

$$E = E_v(v + 1/2) + E_0 J(J+1) + \text{other terms}$$

or in cm^{-1} :

$$\frac{E}{hc} = \omega(v + 1/2) + B J(J+1) + \text{other terms}$$

$$\text{Selection rules: } \Delta v = \pm 1, \pm 2, \pm 3 \dots \pm n$$
$$\Delta J = \pm 1$$

Energy levels of the spectrum are

$$hc\bar{\nu} = E_v n + 2E_0 [J+1, -J]$$
$$= hc\omega n + 2hcB [J+1, -J]$$

where

$$J+1 \text{ corresponds to } \Delta J = +1$$

$$-J \text{ corresponds to } \Delta J = -1$$

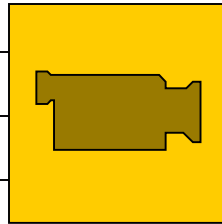
For the fundamental vibration-rotation band of a molecule ($n=1$), the lines are at

$$hc\bar{\nu} = E_v + 2E_0 [J+1, -J]$$
$$= hc\omega + 2hcB [J+1, -J]$$

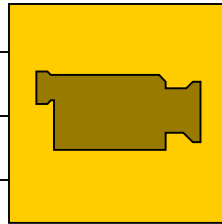
except

that the $J=0$ state cannot have a $\Delta J = -1$ transition.

Vibration-Rotation Spectra



Band Nomenclature



ΔJ selection rules

Main isotope

Isotopologue ^{37}Cl
~24.67% natural abundance

S scaled to values appropriate for atmospheric absorption

Branch/ J	$\text{H}^{35}\text{Cl } 0 \rightarrow 1$		$\text{H}^{37}\text{Cl } 0 \rightarrow 1$		$\text{H}^{35}\text{Cl } 1 \rightarrow 2$		$\text{H}^{37}\text{Cl } 1 \rightarrow 2$		$\text{H}^{35}\text{Cl } 0 \rightarrow 2$	
	$\tilde{\nu}$ (cm^{-1})	Strength	$\tilde{\nu}$ (cm^{-1})	Strength	$\tilde{\nu}$ (cm^{-1})	Strength	$\tilde{\nu}$ (cm^{-1})	Strength	$\tilde{\nu}$ (cm^{-1})	Strength
P 19	2400.401	3.73e-26	2399.077	1.22e-26						
P 18	2429.941	2.24e-25	2428.568	7.33e-26						
P 17	2459.116	1.23e-24	2457.695	3.99e-25					5159.686	2.29e-26
P 16	2487.913	6.08e-24	2486.444	1.98e-24					5198.002	1.14e-25
P 15	2516.318	2.74e-23	2514.802	8.88e-24					5235.347	5.16e-25
P 14	2544.317	1.12e-22	2542.755	3.62e-23					5271.702	2.12e-24
P 13	2571.896	4.12e-22	2570.289	1.33e-22					5307.051	7.84e-24
P 12	2599.041	1.37e-21	2597.39	4.42e-22					5341.379	2.63e-23
P 11	2625.74	4.11e-21	2624.044	1.32e-21					5374.669	7.95e-23
P 10	2651.976	1.11e-20	2650.239	3.57e-21	2554.276	2.00e-26			5406.905	2.16e-22
P 9	2677.738	2.69e-20	2675.959	8.62e-21	2579.393	4.70e-26	2577.759	1.52e-26	5438.072	5.28e-22
P 8	2703.011	5.82e-20	2701.191	1.86e-20	2604.025	9.91e-26	2602.352	3.21e-26	5468.153	1.16e-21
P 7	2727.782	1.12e-19	2725.922	3.59e-20	2628.158	1.87e-25	2626.447	6.04e-26	5497.135	2.25e-21
P 6	2752.036	1.92e-19	2750.138	6.14e-20	2651.779	3.12e-25	2650.03	1.01e-25	5525.001	3.90e-21
P 5	2775.761	2.88e-19	2773.825	9.22e-20	2674.875	4.61e-25	2673.089	1.49e-25	5551.738	5.93e-21
P 4	2798.943	3.76e-19	2796.97	1.20e-19	2697.431	5.92e-25	2695.61	1.91e-25	5577.33	7.84e-21
P 3	2821.569	4.16e-19	2819.561	1.33e-19	2719.435	6.47e-25	2717.581	2.08e-25	5601.764	8.79e-21
P 2	2843.625	3.69e-19	2841.583	1.18e-19	2740.874	5.69e-25	2738.987	1.83e-25	5625.026	7.92e-21
P 1	2865.098	2.22e-19	2863.024	7.08e-20	2761.735	3.40e-25	2759.817	1.09e-25	5647.103	4.84e-21

J lower state values

Hot bands

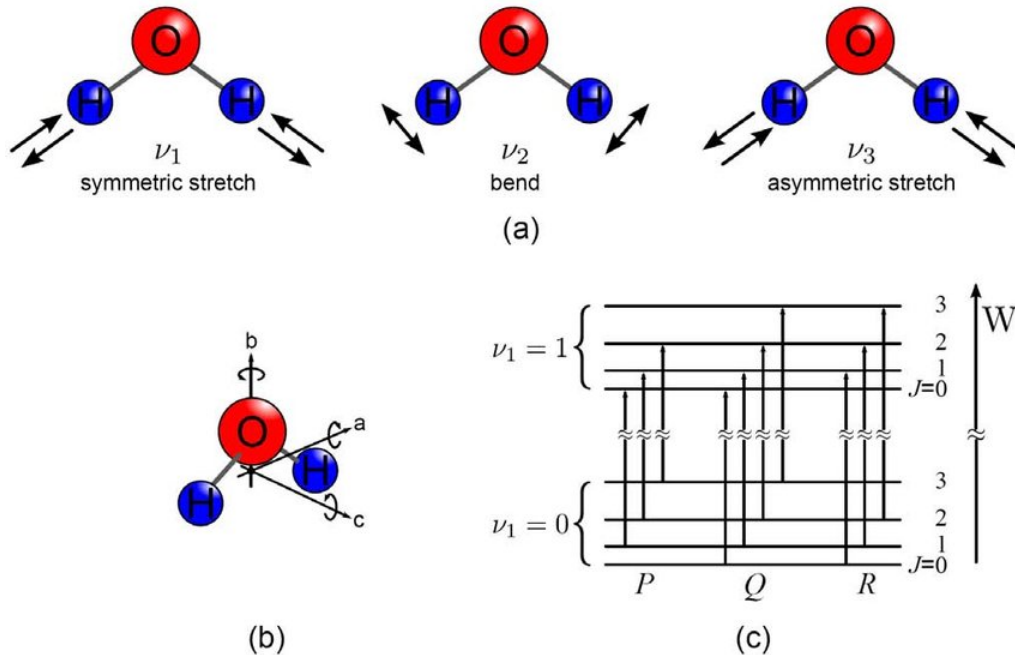
Band positions shift $>$ for first overtone band.

Band centre and line spacing for first overtone are not exactly predicted by “two-term” energy expansion

Branch/ J	$\text{H}^{35}\text{Cl } 0 \rightarrow 1$		$\text{H}^{37}\text{Cl } 0 \rightarrow 1$		$\text{H}^{35}\text{Cl } 1 \rightarrow 2$		$\text{H}^{37}\text{Cl } 1 \rightarrow 2$		$\text{H}^{35}\text{Cl } 0 \rightarrow 2$	
	$\tilde{\nu}$ (cm^{-1})	Strength	$\tilde{\nu}$ (cm^{-1})	Strength	$\tilde{\nu}$ (cm^{-1})	Strength	$\tilde{\nu}$ (cm^{-1})	Strength	$\tilde{\nu}$ (cm^{-1})	Strength
R 0	2906.247	2.37e-19	2904.111	7.55e-20	2801.672	3.60e-25	2799.696	1.16e-25	5687.648	5.34e-21
R 1	2925.897	4.19e-19	2923.732	1.34e-19	2820.724	6.39e-25	2818.72	2.06e-25	5706.092	9.63e-21
R 2	2944.914	5.03e-19	2942.722	1.61e-19	2839.148	7.71e-25	2837.118	2.49e-25	5723.301	1.18e-20
R 3	2963.286	4.85e-19	2961.069	1.55e-19	2856.933	7.49e-25	2854.879	2.41e-25	5739.263	1.16e-20
R 4	2981.002	3.96e-19	2978.76	1.27e-19	2874.067	6.17e-25	2871.99	1.99e-25	5753.966	9.67e-21
R 5	2998.049	2.80e-19	2995.785	8.96e-20	2890.539	4.43e-25	2888.44	1.43e-25	5767.402	7.00e-21
R 6	3014.417	1.75e-19	3012.131	5.58e-20	2906.337	2.80e-25	2904.218	9.05e-26	5779.559	4.46e-21
R 7	3030.094	9.62e-20	3027.789	3.08e-20	2921.45	1.57e-25	2919.314	5.09e-26	5790.427	2.52e-21
R 8	3045.069	4.72e-20	3042.746	1.51e-20	2935.869	7.89e-26	2933.716	2.56e-26	5799.997	1.27e-21
R 9	3059.331	2.07e-20	3056.993	6.65e-21	2949.582	3.55e-26	2947.414	1.15e-26	5808.261	5.70e-22
R 10	3072.872	8.14e-21	3070.518	2.62e-21	2962.58	1.43e-26			5815.209	2.30e-22
R 11	3085.679	2.88e-21	3083.313	9.26e-22					5820.834	8.37e-23
R 12	3097.744	9.15e-22	3095.367	2.95e-22					5825.129	2.74e-23
R 13	3109.057	2.62e-22	3106.671	8.48e-23					5828.066	8.11e-24
R 14	3119.61	6.80e-23	3117.216	2.20e-23					5829.699	2.17e-24
R 15	3129.392	1.59e-23	3126.992	5.17e-24					5829.961	5.25e-25
R 16	3138.396	3.38e-24	3135.993	1.10e-24					5828.867	1.15e-25
R 17	3146.613	6.51e-25	3144.208	2.12e-25					5826.412	2.30e-26
R 18	3154.036	1.14e-25	3151.631	3.72e-26						
R 19	3160.657	1.81e-26								

Polyatomic Molecules: H₂O

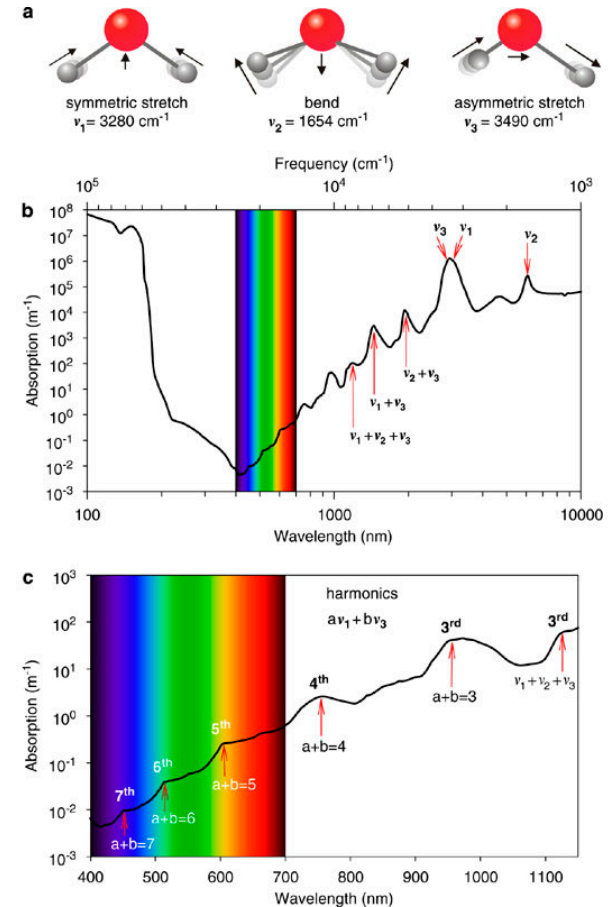
Three normal modes of vibration of H₂O and the resulting infrared bands.



(a) Fundamental vibration modes of the water molecule $\nu_1 = 3657 \text{ cm}^{-1}$, $\nu_2 = 1595 \text{ cm}^{-1}$, and $\nu_3 = 3756 \text{ cm}^{-1}$ [Waewsak, 2004]. (b) Rotational degrees of freedom of the water molecule along with the respective rotational axes. (c) Schematic energy diagram with vibrational states $\nu_1 = 0$ and $\nu_1 = 1$ and rotational states with quantum numbers $J = 0, \dots, 3$. Transitions with $\Delta J = +1$ are denoted as R-branch, transitions with $\Delta J = 0$ are denoted as Q-branch, and transitions with $\Delta J = -1$ are denoted as P-branch [Graybeal, 1988].

Christoph Dyroff, https://www.researchgate.net/figure/a-Fundamental-vibration-modes-of-the-water-molecule-n-1-3-657-cm-1-n-2-1-595-cm-1_fig1_36453728

Maayke Stomp, https://www.researchgate.net/figure/The-three-vibrational-modes-of-the-water-molecule-and-their-fundamental-frequencies-in_fig3_5803530

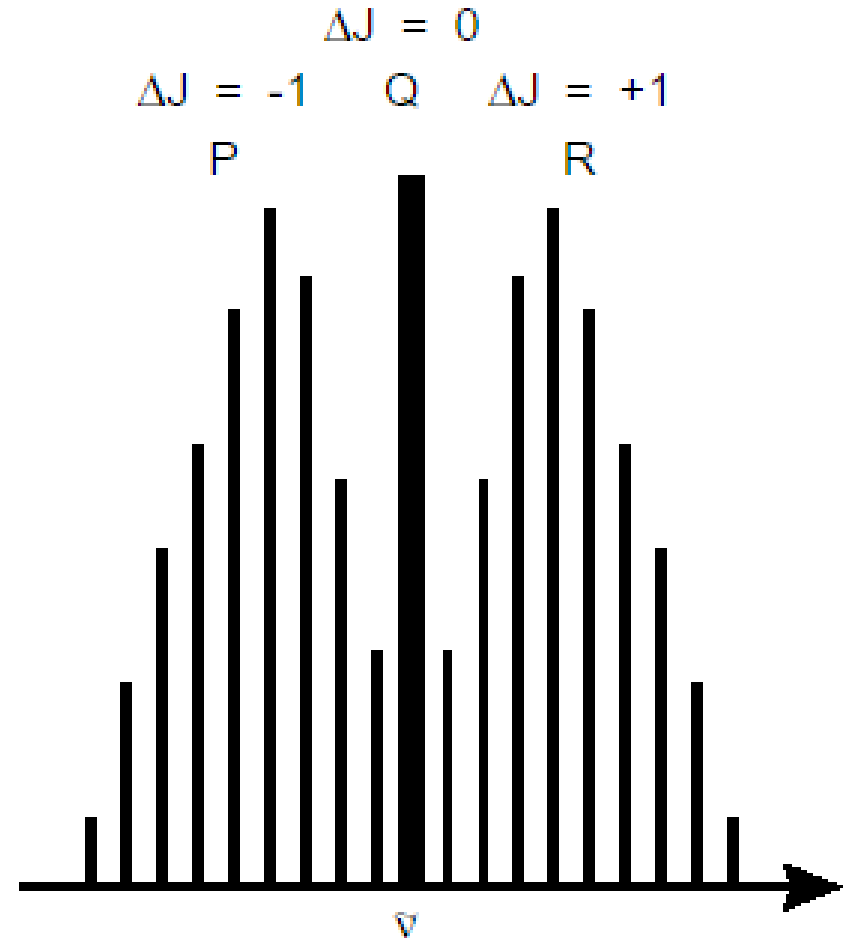
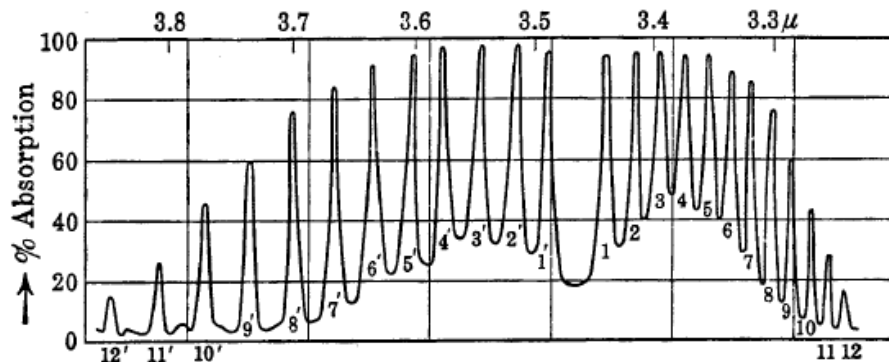


The three vibrational modes of the water molecule and their fundamental frequencies in liquid water: symmetric stretching (ν_1), bending (ν_2) and asymmetric stretching (ν_3). The atoms move in the directions indicated by arrows. (b) Absorption spectrum of pure water (Hale and Querry, 1973; Segelstein, 1981; Pope and Fry, 1997). Peaks in the absorption spectrum correspond to the fundamental frequencies and higher harmonics of the vibrations of the water molecules. (c) Absorption spectrum of pure water in the visible and infrared region. Shoulders in the absorption spectrum correspond to the third, fourth, fifth, sixth and seventh harmonics of the symmetric and asymmetric stretch vibrations, as indicated.

Infrared Absorption Bands - 1

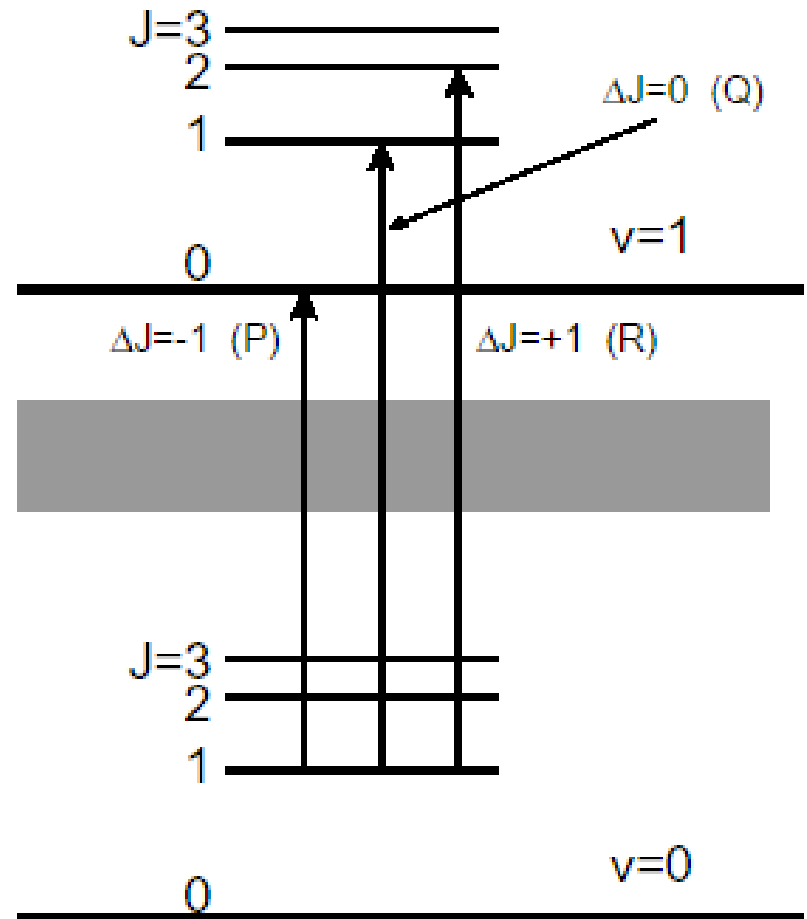
Typical infrared absorption bands are characterized by:

- a central peak – due to the molecule changing its vibrational state (this may or may not exist)
- “humps” – due to the molecule changing both its vibrational and rotational states (composed of many lines).



Infrared Absorption Bands - 2

- The energy diagram shows that:
 - a spectral line on the low wavenumber (energy) side is caused by a decrease in rotational energy ($\Delta J = -1$, where J is the rotational quantum number)
 - a spectral line on the high wavenumber (energy) side is caused by an increase in rotational energy ($\Delta J = +1$)
- Each band is due to the allowed values of the vibrational quantum number v .



Infrared Absorption Bands - 3

- The energy absorption can be written as:

$$hf \propto hc\bar{\nu}_{\text{vib.}} + hc\bar{\nu}_{\text{rot.}}$$

Various bands

Lines within bands

- All the bands of a given gas have similar bands, as they share the same rotational wavenumbers $\bar{\nu}_{\text{rot.}}$
- The large central peak is caused by the $\nu_{\text{vib.}}$ being slightly affected by the rotational state and therefore even if the rotational state does not change there are slight differences in the absorption energy for different vibrational states.

Infrared Absorption Bands - 4

- Cold band – the lower state of the transition is the ground state.
- Hot band – the lower state is some other state (not ground state).
 - These are generally much weaker and very temperature dependent because the lower state population varies with $\exp(-hc\bar{\nu}_v / kT)$
- Each infrared band consists of spectral lines
 - This means that the monochromatic absorption coefficient k_a varies wildly in a very short distance in wavenumber space.
 - A typical band may contain about 2000 significant lines, as well as many weak lines.
 - This makes the calculation of total absorption and heating rates very complex!

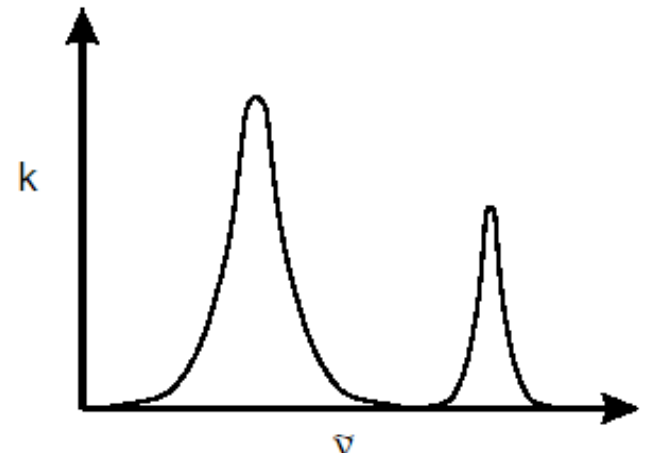


Figure 54: Typical k for a molecule

Vibration-Rotation Band Absorption

- Accurate determination of the absorption of a band can require a complex calculation.
- Independent line approximation
 - Applicable if the absorptions of individual lines do not overlap.
 - Each line has its own equivalent width.
 - The band absorption is just the sum of the individual lines.
- In the case of overlapping absorptions – the band absorption is different from the sum of the absorptions of the lines.

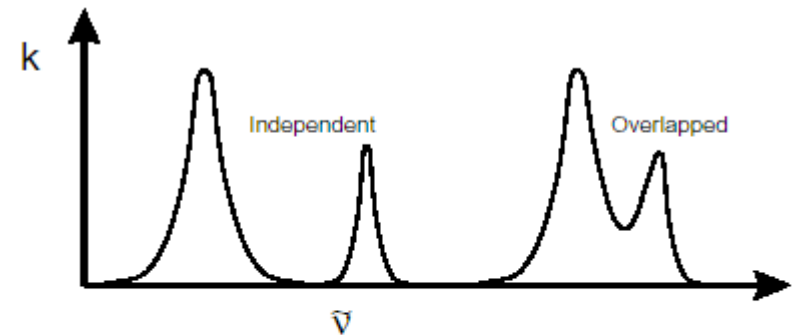


Figure 57: Effect of Overlapping Lines can vary

Width and Shape of Spectral Lines

