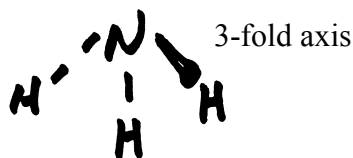


11. Symmetric top molecules

Bernath, Chapters 6 and 7; **Davidson**, Chapter 11, for more detail; **Herzberg**, *Infrared and Raman Spectra*, for yet more detail.

Two rotational constants are the same. This usually (not always) requires 4 atoms at minimum.



Symmetric top, but rare
(astrophysical H_3^+)



Not symmetric tops

Prolate: $A > B = C$

Oblate: $A = B > C$ (much less common)



Thanks, S. Novick!

A is the largest rotational constant, C the smallest.

$$E(\text{prolate}) = BJ(J+1) + (A-B)K^2 - D_J J^2(J+1)^2 - D_{JK} J(J+1)K^2 - D_K K^4 + \dots$$

Selection rules: $\Delta J = \pm 1$, $\Delta K = 0$ (like discrete diatomic manifolds)

$$\text{Partition function: } Q \approx \frac{\pi^{1/2}}{s} \left(\frac{T}{c_2 A} \right)^{1/2} \left(\frac{T}{c_2 B} \right), \quad s \equiv \text{symmetry number}$$

12. Asymmetric top molecules

They have a quite complex energy expression (can \equiv a basis set of symmetric top wave functions to diagonalize the Hamiltonian).

$$Q \approx \pi^{1/2} \left(\frac{T}{c_2 A} \right)^{1/2} \left(\frac{T}{c_2 B} \right)^{1/2} \left(\frac{T}{c_2 C} \right)^{1/2}$$

Some of the rotational degrees of freedom for nonlinear polyatomics can be hydrogenic, as for HX molecules. Examples include HO_2 , H_2O , H_2O_2 , HOCl , HOBr , and NH_3 . For HO_2 , the rotational constants are $A = 20.357 \text{ cm}^{-1}$, $B = 1.118 \text{ cm}^{-1}$, $C = 1.056 \text{ cm}^{-1}$. A has a hydrogenic value.

A rigid planar molecule (or any rigid planar object) will have $I_C = I_A + I_B$ (easy to demonstrate using the Pythagorean theorem). The *inertial defect* measures the departure from this, defined as $\Delta = I_C - I_A - I_B$. Non-zero inertial defect is caused by vibrational averaging and/or (for tetratomic or greater molecules) out-of-plane bending vibrations.

13. Polyatomic vibrations, briefly:

For a nonlinear N -atomic molecule there are $3N-6$ vibrational *degrees of freedom* (= number of vibrational fundamentals). This comes from 3 degrees of freedom, for the 3 spatial directions, from each atom, -3 for molecular translation, -3 for molecular rotations. For a linear polyatomic there are $3N-5$, plus vibrational angular momentum, which gives rise to *l-type doubling*.

Example for triatomic isosceles XY_2 molecule (C_{2v} symmetry) $S_1 = \nu_1$: symmetric stretch; $S_2 = \nu_2$: bend; $S_3 = \nu_3$: asymmetric stretch (From Herzberg, *Infrared and Raman Spectra*).

Examples (HITRAN2008):

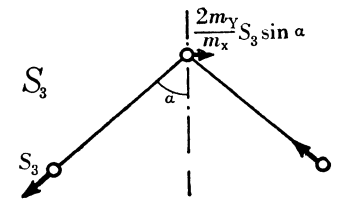
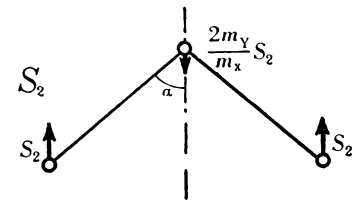
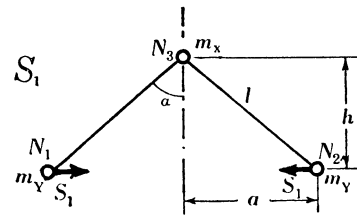
	ν_1	ν_2	ν_3
H ₂ O	3652 cm ⁻¹	1595 cm ⁻¹	3756 cm ⁻¹
O ₃	1103 cm ⁻¹	701 cm ⁻¹	1042 cm ⁻¹

also, O₃ 2 ν_1 @ 2201; 2 $\nu_1 + \nu_2$ 2886; 3 ν_1 @ 3278 ...

CO₂ has 4 fundamentals (since it is linear): symmetric and asymmetric stretch and *doubly-degenerate* bending. The symmetric stretch is *Raman* active rather than infrared active, that is, the transition is allowed by the anisotropy of the polarizability rather than by a dipole moment derivative (since it is, by symmetry, non-existent). The polarizability is responsible for molecular (Rayleigh) scattering. Its anisotropy causes part of the scattering (4% for air) to be *inelastically* scattered. The scattered photons gain or lose energy (becoming bluer or redder) while the molecules lose or gain rovibrational energy, respectively. More later on the atmospheric importance (you could check out our paper *Ring effect studies: Rayleigh scattering, including molecular parameters for rotational Raman scattering, and the Fraunhofer spectrum*, K. Chance and R.J.D. Spurr, *Appl. Opt.* **36**, 5224-5230, 1997, available at <http://cfa-www.harvard.edu/atmosphere/publications.html>). See *Bernath* for details on the physics, Herzberg for many more details.

ν_1 (symmetric) 1286 cm⁻¹
 ν_2 (greenhouse) 667 cm⁻¹; doubly degenerate
 ν_3 (strong, asymmetric) 2349 cm⁻¹

The full story for CO₂ is, of course, much more complicated. See, for example, Herzberg, *Infrared and Raman Spectra*, Table 56 and Figure 84.



For a list of *characteristic vibrational band frequencies* – see Table 7.5 in *Bernath* (e.g., CO ~ 1700 cm⁻¹).