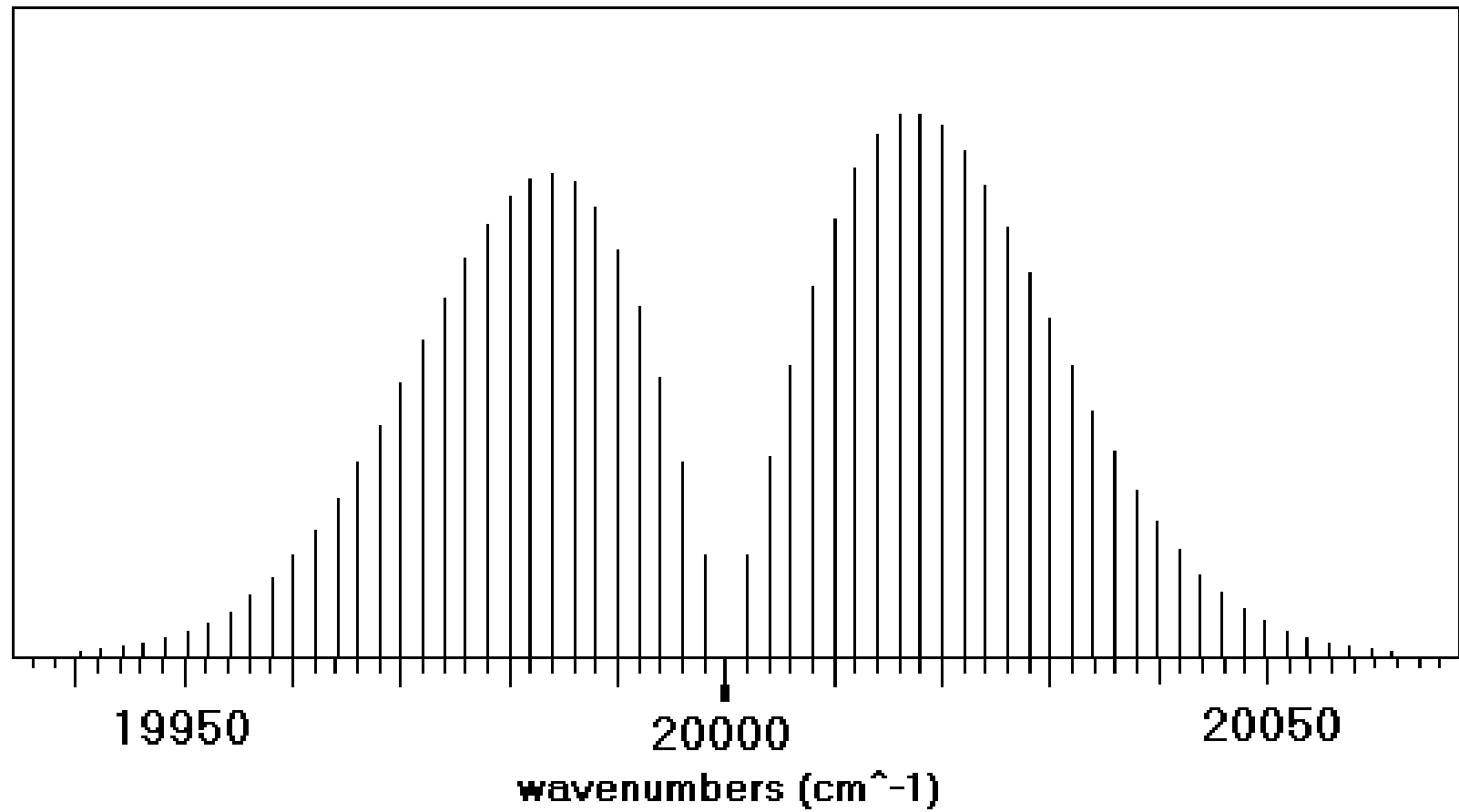
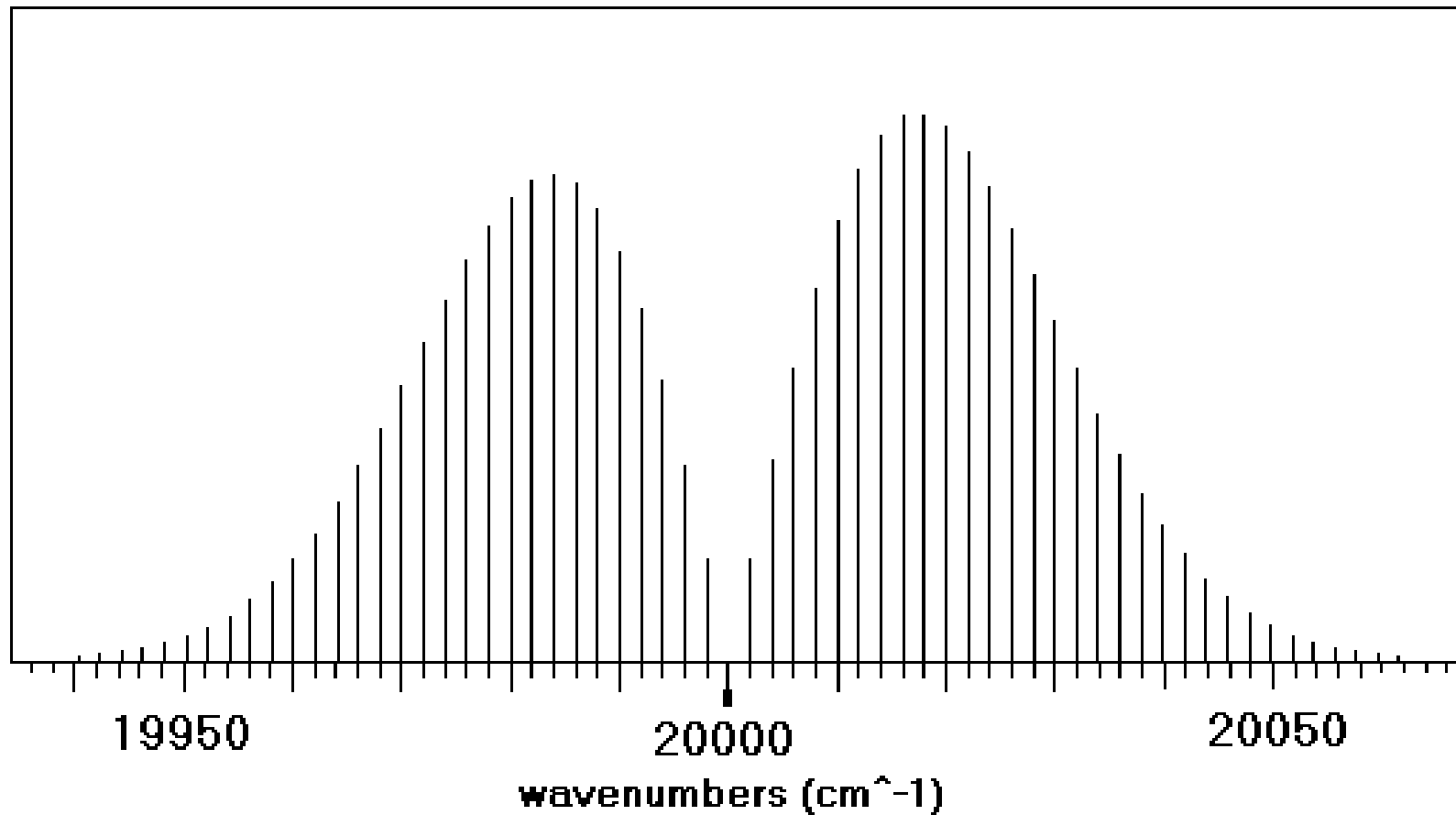


A Pictorial representation of Rotational Band Structure.

You might see these bands as part of a series (progression) in an electronic transition, or 'alone' in an IR/Raman transition. They also may come in 'stacks' (polyatomic), where transitions differing by just K are close in energy.

Let's look at a single band at a time, and see how they can look (ideally)



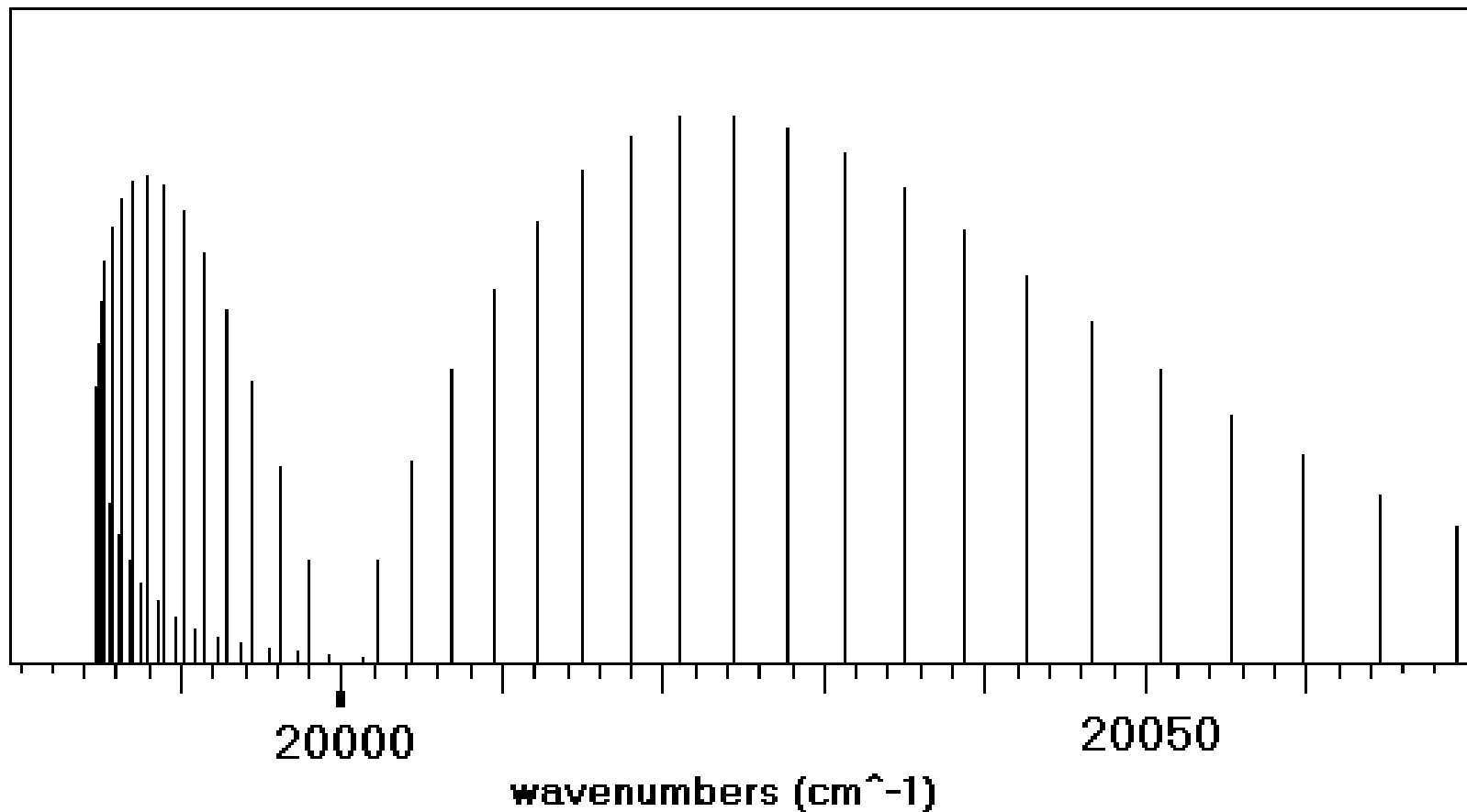


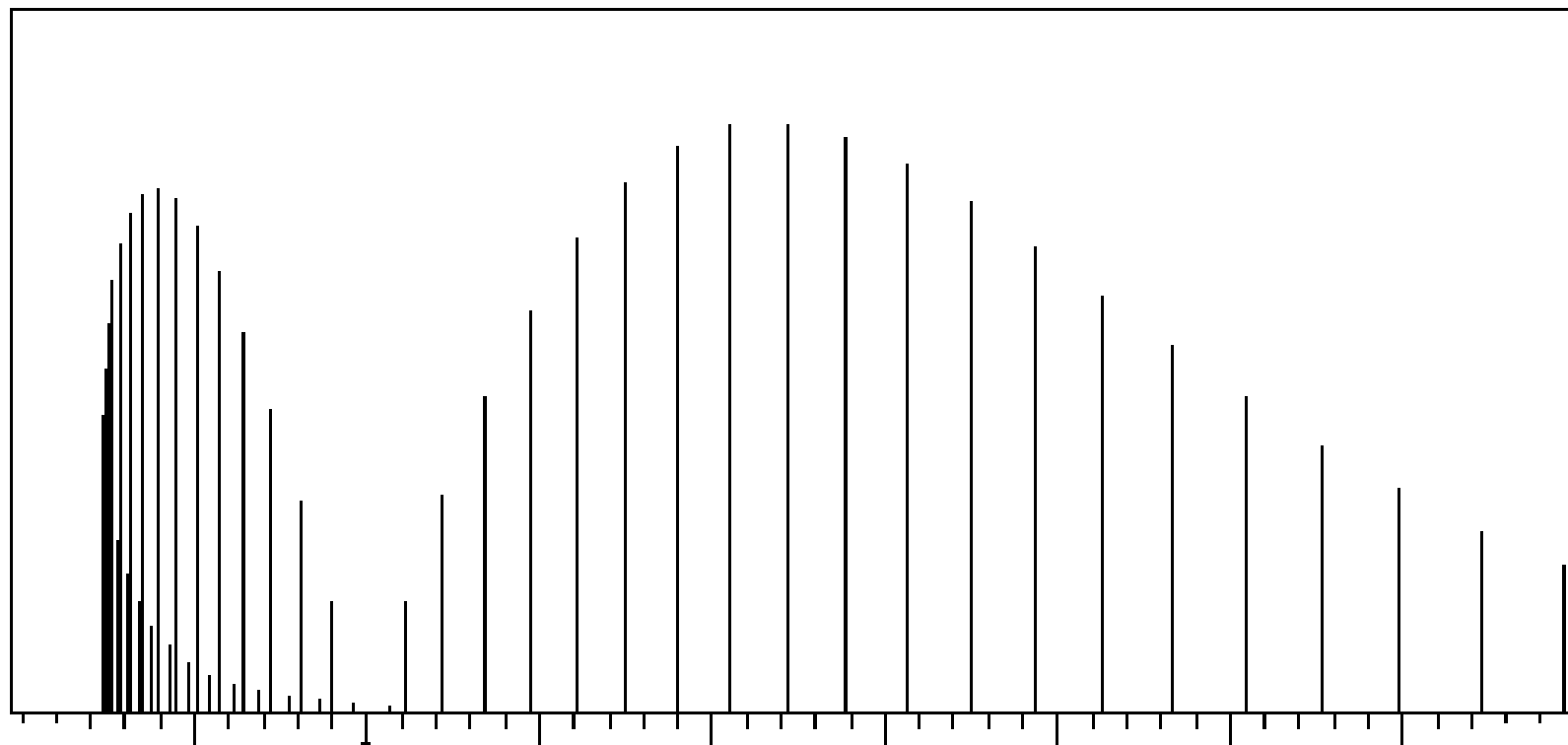
What can I see?

$$K' = K'' = 0$$

$$\nu_0 = 20000$$

$$B' = B'' = 1.00 \text{ cm}^{-1}$$





20000

20050

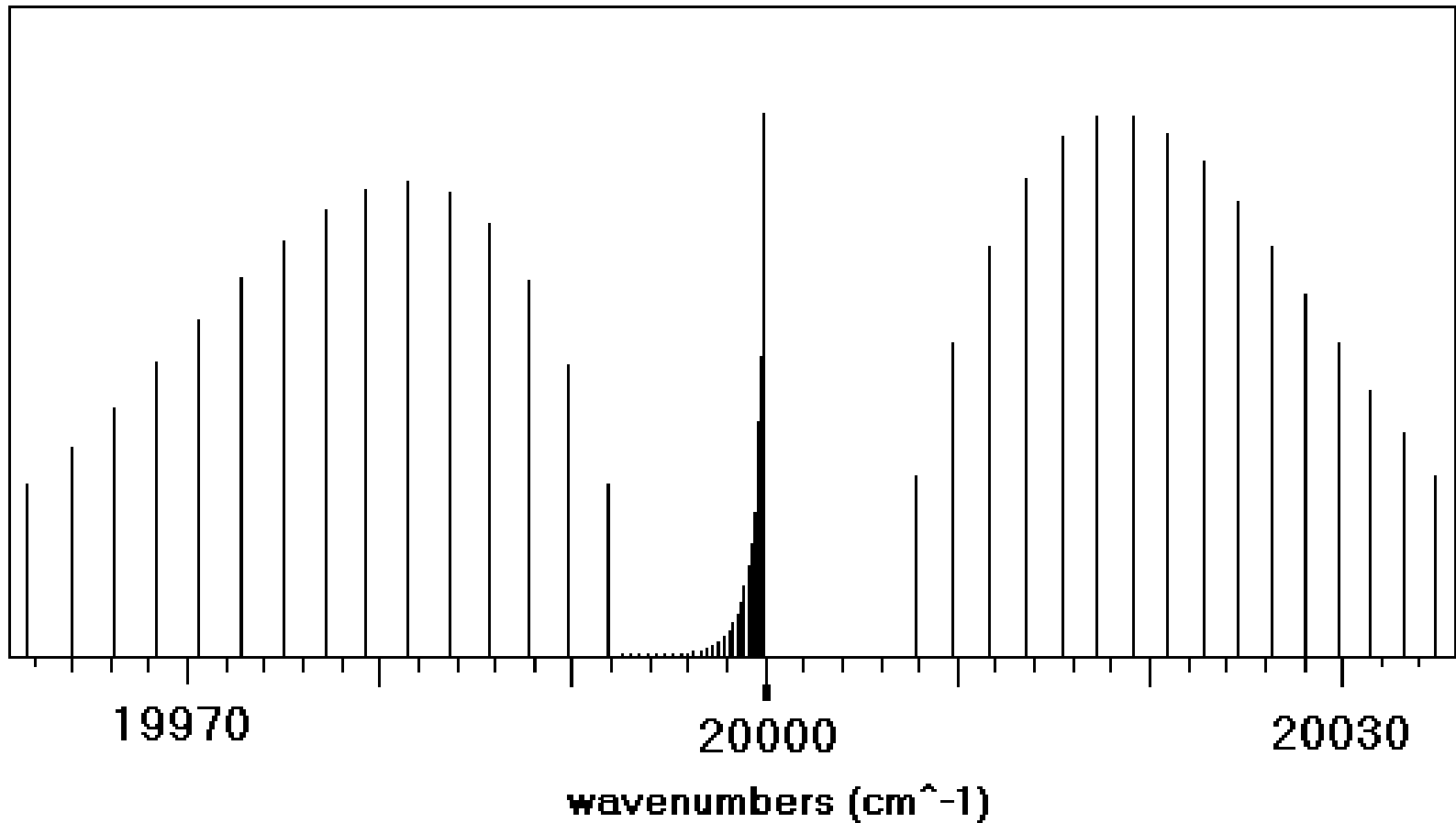
wavenumbers (cm⁻¹)

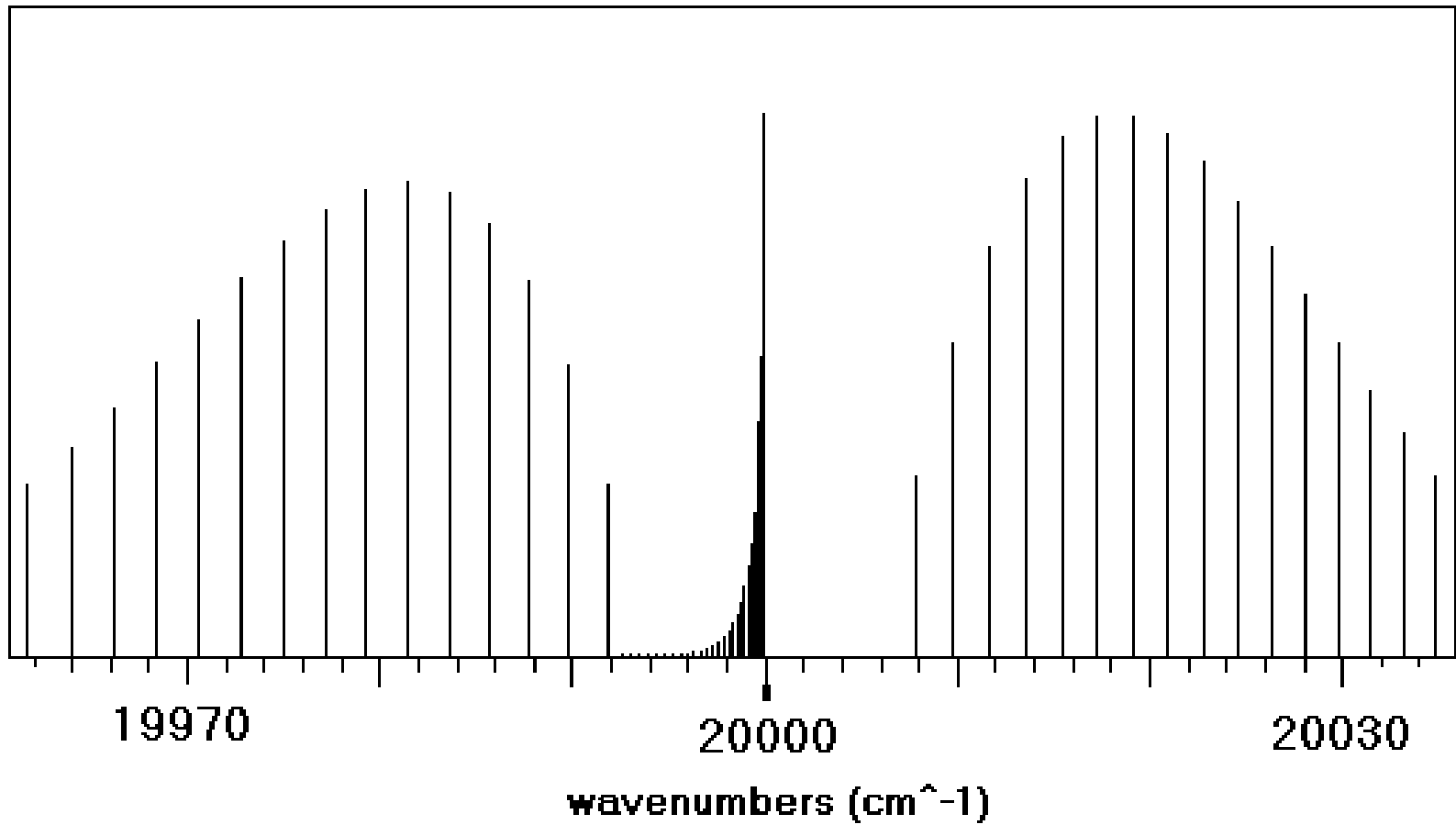
What can I see?

$K'=K''=0$

$\nu_0 = 20000$

$B' > B''$



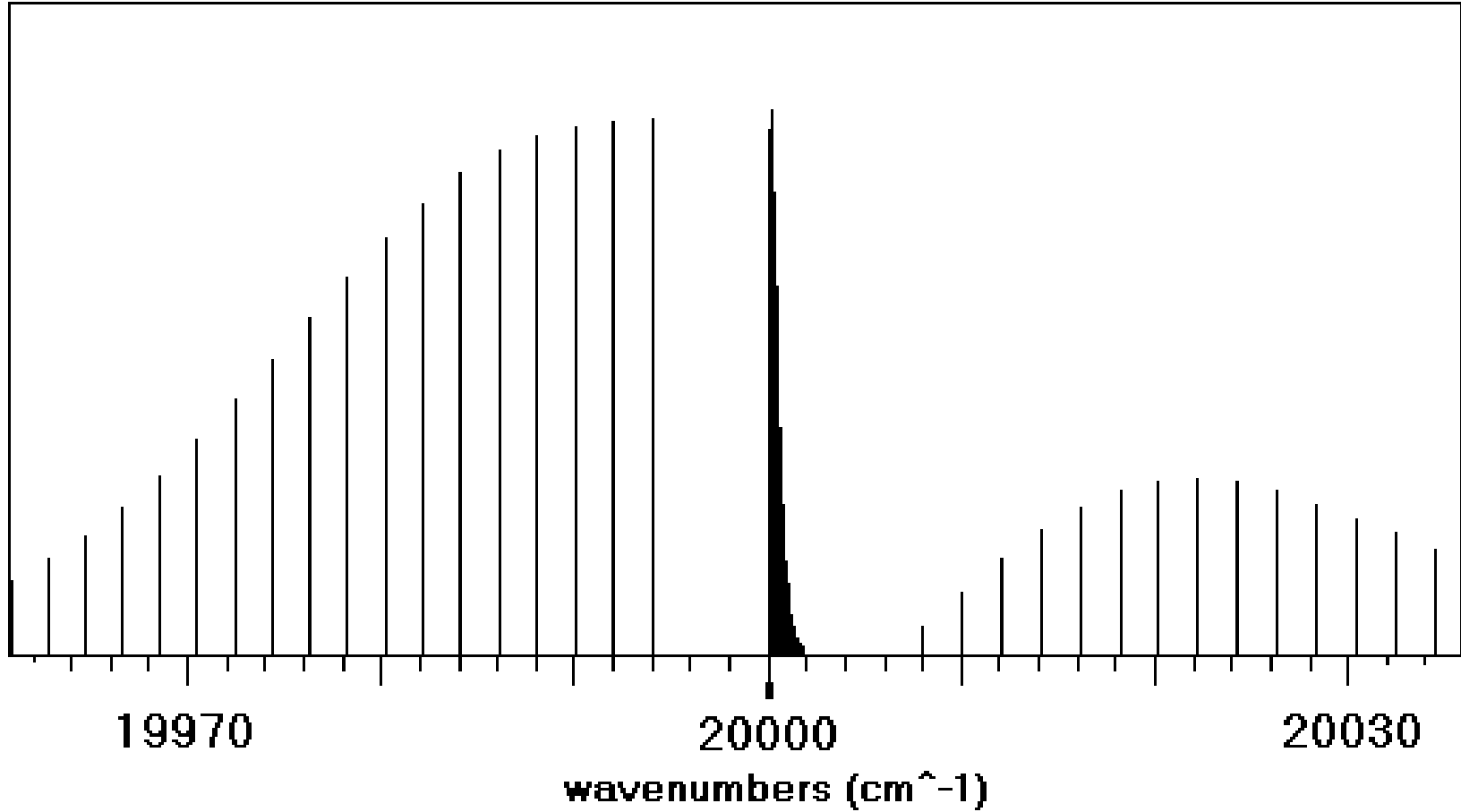


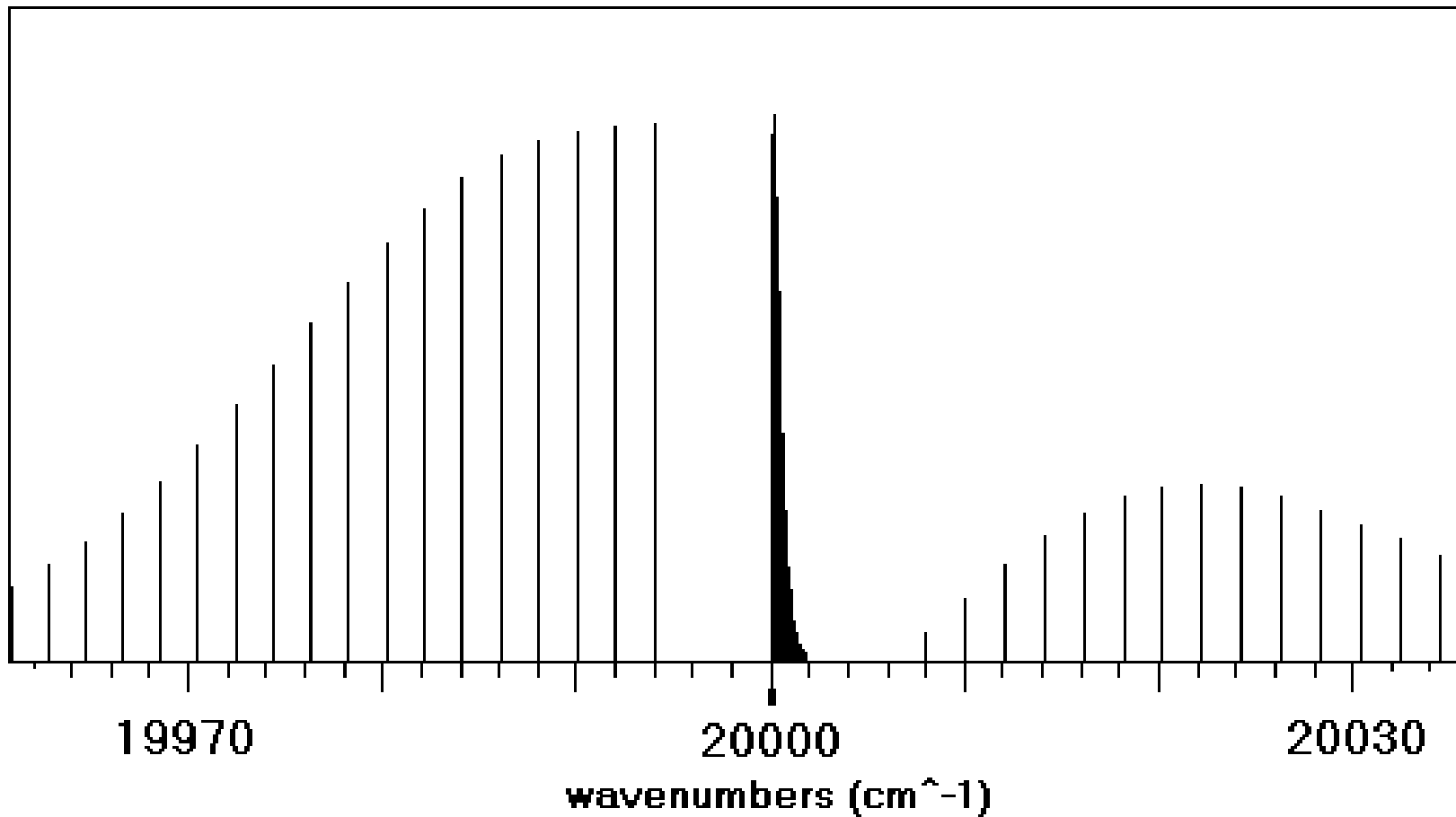
What can I see?

$K'=K''=3$ (parallel transition)

$\nu_0 = 20000$

$B' < B''$ (slightly)





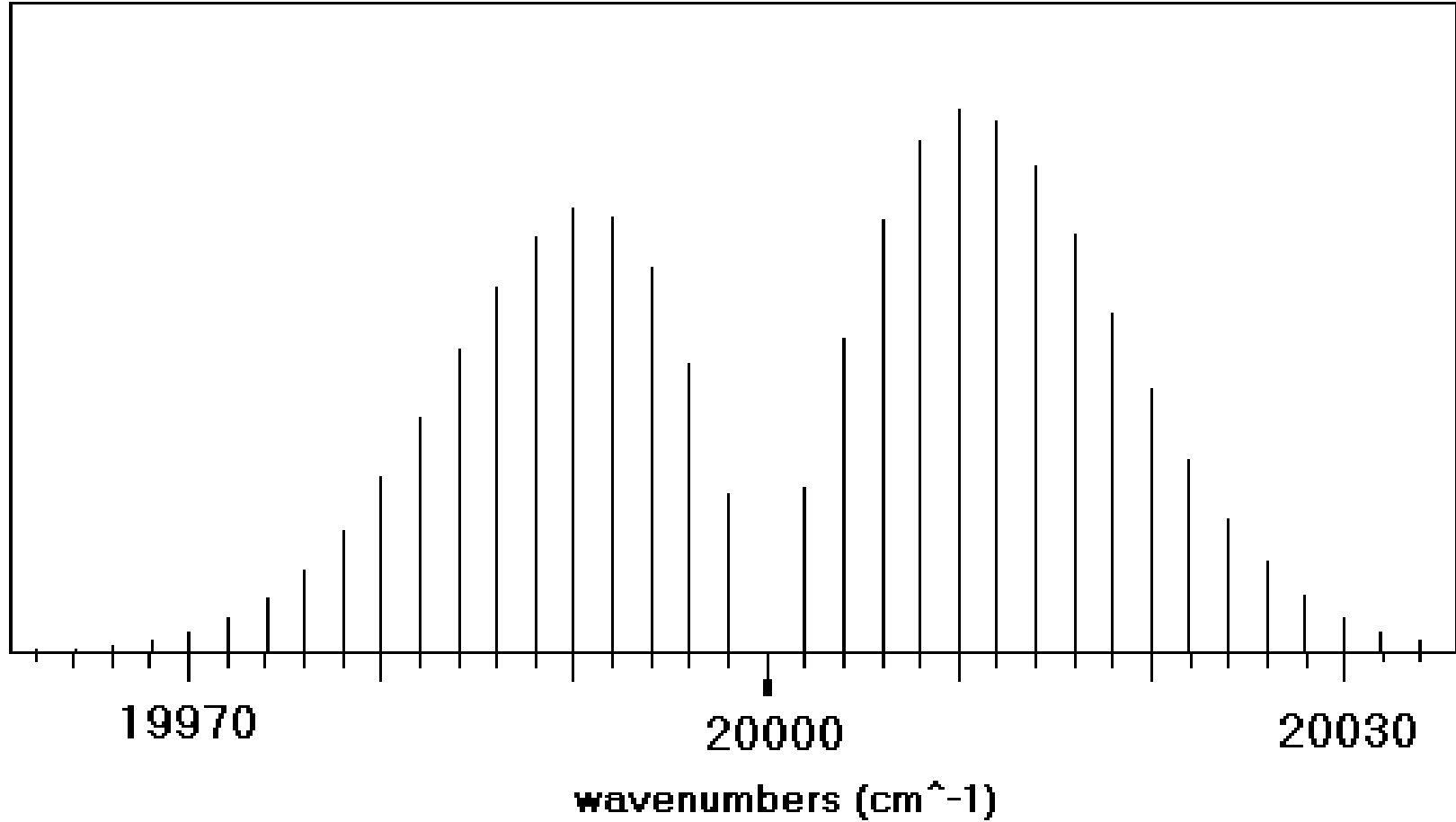
What can I see?

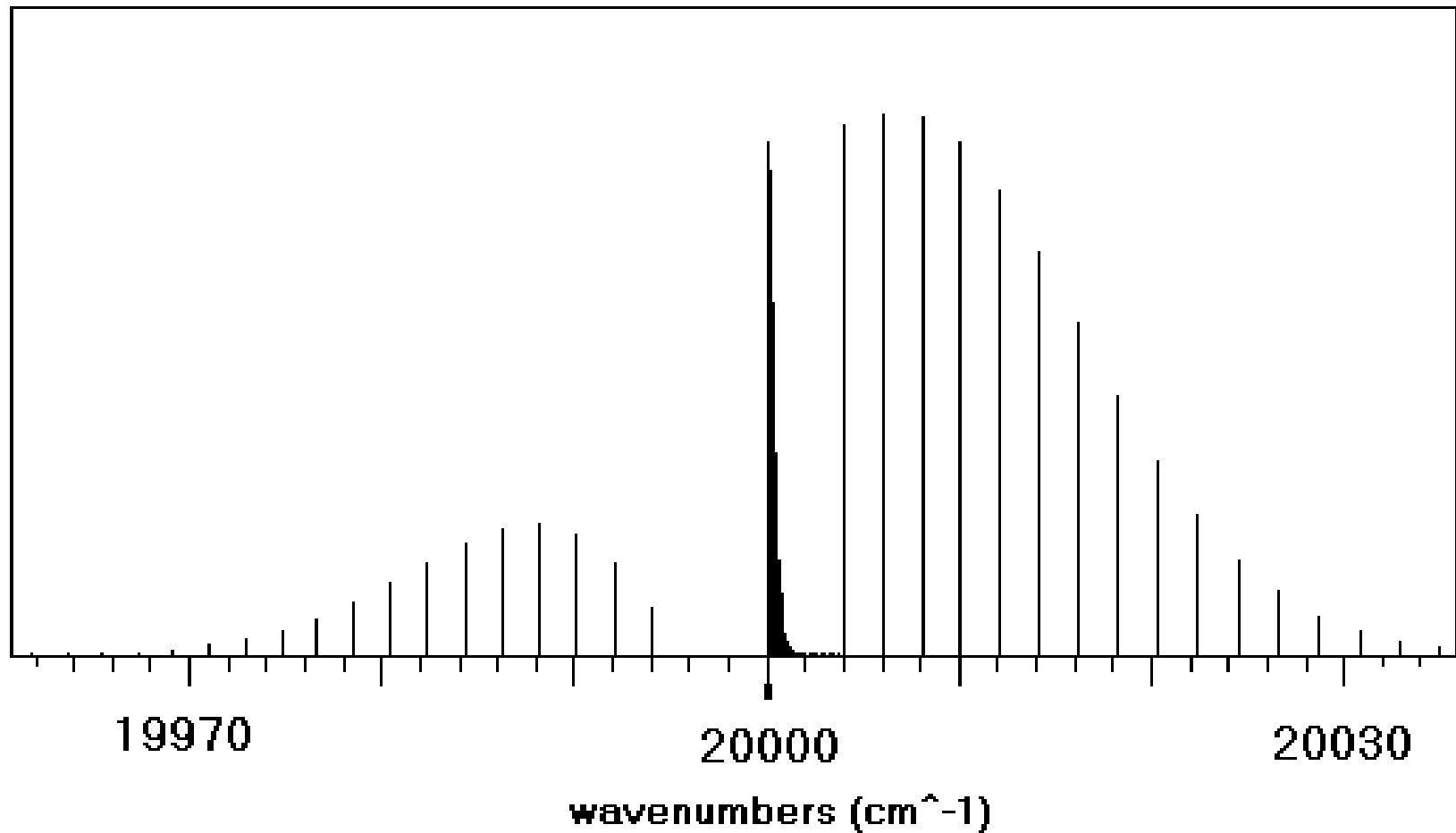
$$K' = K'' - 1$$

$$K'' = 3$$

$$\nu_0 = 20000$$

$$B' > B'' \text{ (slightly)}$$





$$B_e \equiv \text{EQUILIBRIUM ROTATIONAL CONSTANT}$$

$$= \frac{h}{8\pi^2 M r_e^2 c} \quad (\text{in cm}^{-1})$$

(BOND) STRETCHES WITH v !

$$B_v = B_e - \alpha_e (v + 1/2)$$

VIBRATION-ROTATION COUPLING!

$$\alpha_e = \frac{6 (\omega_e x_e B_e^3)^{1/2}}{\omega_e} \quad \text{(PERKINS)} \quad - \quad \frac{6 B_e^2}{\omega_e}$$

For the Morse Oscillator (Not Rigid Rotor / Harmonic Oscillator)

$$F(J) + G(v) = \omega_e \left(v + \frac{1}{2} \right) - \omega_e x_e \left(v + \frac{1}{2} \right)^2 + \left(B_e - \alpha_e \left(v + \frac{1}{2} \right) \right) J(J+1) - D_{cd} \left(J(J+1) \right)^2$$

D_{cd} = CENTRIFUGAL DISTORTION

$$D_{cd} \approx 4 B_e^3 / \omega_e^2 \quad (\text{KRATZER})$$

EVEN THE SHO HAS CENT DISTORTION!

Now all transitions between two electronic states (described by Morse Potentials), or, within one electronic state (rotational, or ro-vibrational), can be calculated (indirectly) from the potential parameters!

{Many lines from a handful of constants}

Even Isotopomers of the same molecule can be calculated without additional (adjustable) parameters

(most of the time)

CONSIDER TWO ISOTOPE

μ REDUCED MASS OF
MAJOR ISOTOPE

μ^I REDUCED MASS OF
MINOR ISOTOPE

$$\rho = \sqrt{\frac{\mu}{\mu^I}}$$

$$G_v^I = \rho \omega_e (v + \frac{1}{2}) - \rho^2 \omega_e x_e (v + \frac{1}{2})^2 + \rho^3 \omega_e y_e (v + \frac{1}{2})^3$$

BUT FOR ROTATION

$$B_v^I = \rho^2 B_v ; A_v^I = \rho^2 A_v$$

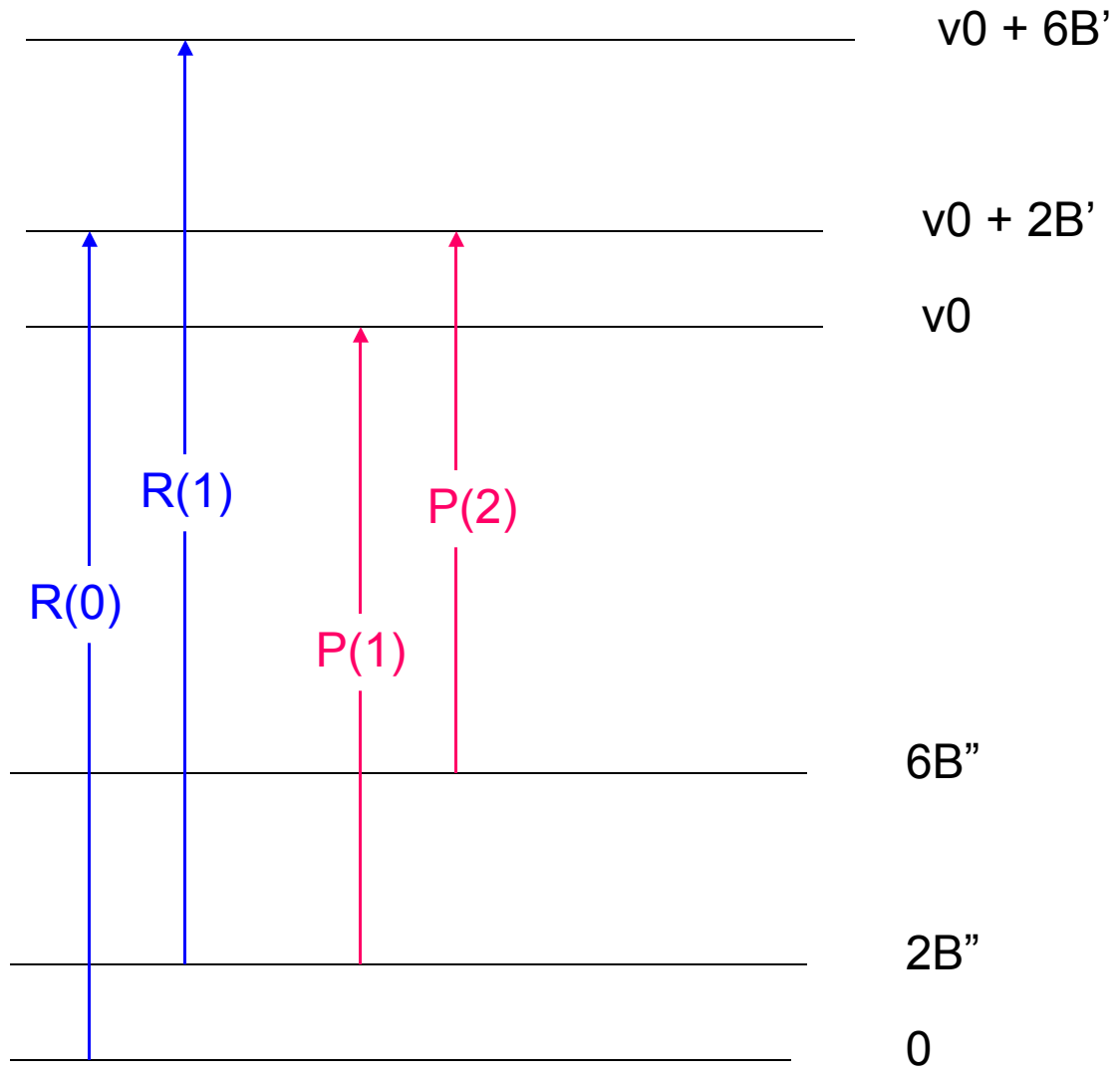
1.5 $F_v^I = \rho^2 B_v J(J+1) + \rho(A - B) K^2 = \rho^2 F_v(J, K)$

HW#11 has a conceptual problems which involve understanding ro-vibronic transitions.

Perhaps you need help?

Prob #1-#4 (from Atkins EOC) read up

Prob #5: Here is the 'picture' you should be thinking about...



HW#11 Prob # is a numerical problem which involves understanding the Morse Potential.

Please use an Excel spreadsheet or other programmable aid!

Here are some hints regarding the numbers that you should be getting....

	$h =$	$6.6260800 \times 10^{-34}$	Js	Fundamental
	$c =$	2.9979246×10^{10}	cm/s	Fundamental
	$N_A =$	6.0221400×10^{23}	mol ⁻¹	Fundamental
Given	$D =$	2.0000	eV	
	$D =$	1.6131080×10^4	cm ⁻¹	
	$D =$	$3.2043565 \times 10^{-19}$	J	
	$\beta =$	1.0503411×10^{10}	m ⁻¹	
	$\beta =$	1.0503	Ångstroms ⁻¹	
Given	$r_e =$	2.0000	Ångstroms	
	$r_e =$	2.0000×10^{-10}	m	
Given	$\mu =$	30.0000	amu	
	$\mu =$	$4.9816178 \times 10^{-26}$	kg	
Given	$\omega_e =$	200.0000	cm ⁻¹	
	$\omega_e =$	5.9958492×10^{12}	Hertz	
	$\omega_e =$	3.7673031×10^{13}	radians/s	

The results of the Morse Analysis should give you these Spectroscopic Constants, from which you can calculate all the Transition Frequencies...

$$\omega_e = 200.000 \text{ cm}^{-1}$$

$$\omega_e X_e = 0.619921 \text{ cm}^{-1}$$

$$B_e = 0.140480 \text{ cm}^{-1}$$

$$D_{CD} = 2.772347 \times 10^{-7} \text{ cm}^{-1}$$

$$\alpha_e = 6.516507 \times 10^{-4} \text{ cm}^{-1}$$

Fin