

Both  $\text{Cl}_2$  and  $\text{HCl}$  are in the first excited rotational state ( $i=1$ ). Compare their rotational energies.

(assume the  $^{35}\text{Cl}$  isotope in both cases)

$$\mu(\text{Cl}_2) = \frac{(35.0)^2 \text{amu}^2}{2(35.0) \text{amu}} = \underline{17.5 \text{amu}}$$

$$\mu(\text{HCl}) = \frac{(1.0 \text{amu})(35.0) \text{amu}}{(1.0 + 35.0) \text{amu}} = \underline{0.972 \text{amu}}$$

$$R_0(\text{Cl}-\text{Cl}) = 1.988 \text{ \AA} \quad \text{and} \quad R_0(\text{H}-\text{Cl}) = 1.275 \text{ \AA}$$

(picometers, my funny!)

$$\frac{E_{\text{rot}}(\text{HCl})}{E_{\text{rot}}(\text{Cl}_2)} = \frac{\mu(\text{Cl}_2) R_0^2(\text{Cl}_2)}{\mu(\text{HCl}) R_0^2(\text{HCl})} = \left( \frac{17.5 \text{amu}}{0.972 \text{amu}} \right) \left( \frac{1.988 \text{ \AA}}{1.275 \text{ \AA}} \right)^2 = \boxed{44}$$

(try to use proportionalities whenever possible!)

H-Cl is lighter and shorter, which makes it easier to spin around (i.e. more  $E_{\text{rot}}$ )

And, since  $\Delta E_{\text{rot}} \propto \frac{1}{\mu R_0^2}$ , also true that HCl's energy levels are spaced further apart

## Exploring $\Delta E_{rot}$ :

- (1) Calculate  $\Delta E_{rot}$  for the  $i=1$  to  $i=2$  transition in  $H-^{35}Cl$  and  $^{35}Cl_2$

**HCl**

In general, 
$$E_{rot} = i(i+1) \frac{h^2}{8\pi^2} \left( \frac{1}{\mu R_0^2} \right)$$

$$E_{rot}(i=1) = \frac{1(2)}{8\pi^2} (6.626 \times 10^{-34})^2 \frac{J^2 s^2}{part^2} \left( \frac{1}{0.972 amu} \right)$$

$$\times \left( \frac{1}{(1.275)^2 \cancel{A^2}} \right) \left( \frac{1}{1.661 \times 10^{-27} \cancel{kg part^{-1}}} \right)$$

$$\times \left( \frac{\cancel{J^2}}{10^{-20} \cancel{m^2}} \right) \left( \frac{\cancel{kg m^2 s^{-2}}}{J} \right)$$

**$E_{rot}(i=1) = 4.2_{37} \times 10^{-22} J part^{-1}$**

We don't need to re-write this calc 3 more times...

	$i=1$	$i=2$	$\Delta E_{rot}$
HCl	$4.2_{37} \times 10^{-22}$	$1.2_{71} \times 10^{-21}$	$8.5 \times 10^{-22}$
Cl <sub>2</sub>	$9.6_{80} \times 10^{-24}$	$2.9_{04} \times 10^{-23}$	$1.9_4 \times 10^{-23}$

(all E's in J particle<sup>-1</sup>)

Indeed,  $\Delta E_{rot}$  bigger for HCl

- (2) What frequency (and kind) of light would excite Cl<sub>2</sub> rotationally?

$$\Delta E_{rot} = h \nu_{photon}$$

$$\nu_{photon} = \frac{1.9_4 \times 10^{-23} J part^{-1}}{6.63 \times 10^{-34} J \cdot s \cdot part^{-1}} = \boxed{2.9 \times 10^{10} Hz}$$

Calculate  $\nu$  and  $\Delta E_{\text{vib}}$  for H-H and D-D.

Assume both molecules have  $k_f = 570. \text{ kg s}^{-2}$ .

$$\mu(\text{H}_2) = \frac{(1.0 \text{ amu})(1.0 \text{ amu})}{(1.0 + 1.0) \text{ amu}} = \underline{0.50 \text{ amu}}$$

$$\text{so } \nu = \frac{1}{2\pi} \sqrt{\frac{k_f}{\mu}}$$

$$= \frac{1}{2\pi} \sqrt{\left(\frac{570. \text{ kg}}{\text{s}^2}\right) \left(\frac{1}{0.50 \text{ amu}}\right) \left(\frac{\text{amu}}{1.661 \times 10^{-27} \text{ kg}}\right)}$$

$$\boxed{\nu = 1.3_2 \times 10^{14} \text{ s}^{-1}}$$

What kind of light would excite vibrations?

$$\text{and } \Delta E_{\text{vib}} = h\nu = (6.626 \times 10^{-34} \text{ J} \cdot \text{particle}^{-1}) (1.3_2 \times 10^{14} \text{ s}^{-1})$$

Just like Einstein's photon formula!

$$\boxed{\Delta E_{\text{vib}} = 8.7_5 \times 10^{-20} \text{ J particle}^{-1}}$$

$$\mu(\text{D}_2) = \frac{(2.0 \text{ amu})(2.0 \text{ amu})}{(2.0 + 2.0) \text{ amu}} = \underline{1.0 \text{ amu}} = 2\mu(\text{H}_2)$$

Do calculation by using proportionalities!

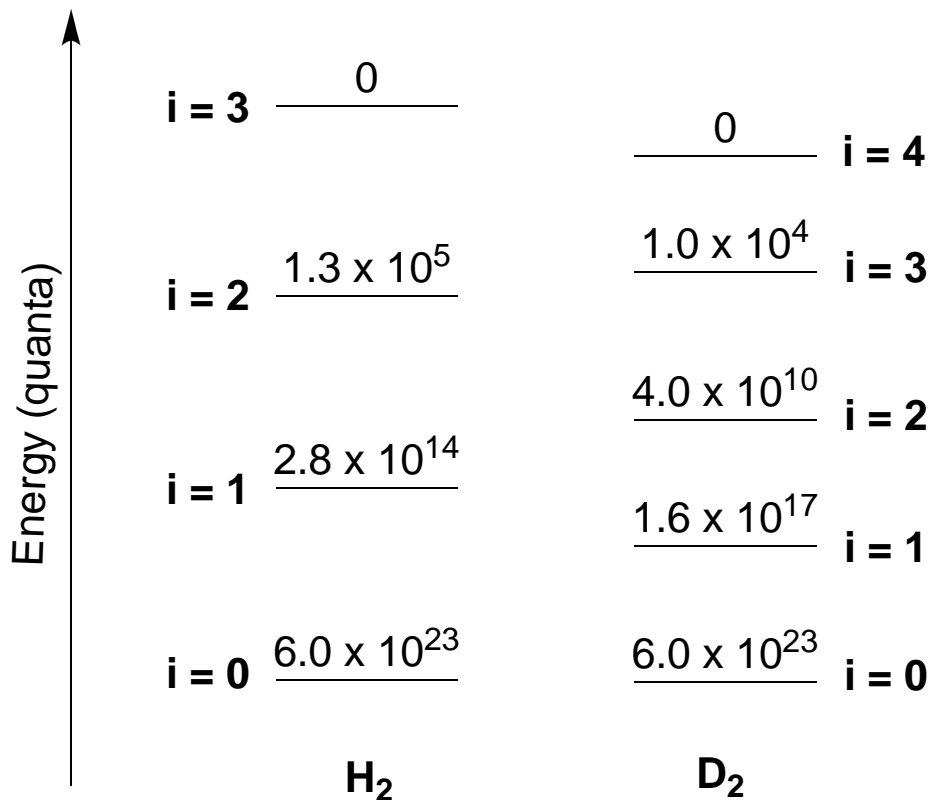
$$\frac{\nu(\text{D}_2)}{\nu(\text{H}_2)} = \frac{\sqrt{\frac{k_f}{\mu(\text{D}_2)}}}{\sqrt{\frac{k_f}{\mu(\text{H}_2)}}} = \sqrt{\frac{\mu(\text{H}_2)}{\mu(\text{D}_2)}} = \sqrt{\frac{0.50 \text{ amu}}{1.0 \text{ amu}}} = 0.70_7$$

$$\text{so } \nu(\text{D}_2) = (0.70_7) (1.3_2 \times 10^{14} \text{ s}^{-1}) = \boxed{9.3_3 \times 10^{13} \text{ s}^{-1}}$$

$$\text{and } \Delta E_{\text{vib}} = h\nu = \boxed{6.1_8 \times 10^{-20} \text{ J particle}^{-1}}$$

What is the most probable distribution of vibrational energy at 298 K?  
 (Assume we have 1.0 mol of H<sub>2</sub> or 1.0 mol of D<sub>2</sub>.)

The Boltzmann equation predicts the following energy level population diagrams (energies are to scale):



Same temperature => same amount of thermal energy in each system

But the energy is more "spread out" in the 1.0 mol of D<sub>2</sub>--why?

## Ways to Store Energy in Matter: A Summary

Type of Energy	$\Delta E$ (J)	Type of Light Matching $\Delta E$	How Many Levels Populated at 298 K?
Electronic	$10^{-18}$	UV/Visible	1
Vibrational	$10^{-20}$	Infrared	~5
Rotational	$10^{-23}$	Microwave	~500
Translational (in ~1 L box)	$10^{-40}$	<u>Long-Wave</u> Radio	~ $10^{20}$

Going down the table → increasing effectiveness in dispersing energy