1. The bonding in H_2 and D_2 is identical as they only differ in the number of neutrons.

(a) What is the *ratio* of the reduced masses for the H_2 and D_2

The reduced mass is given by:

$$\mu = \frac{m_1 \times m_2}{m_1 + m_2}$$

For H_2, $m_1 = m_2 = 1$ g mol^{-1} so $\mu = \frac{1 \times 1}{1+1}$ g mol^{-1} = ½ g mol^{-1}.

For D_2, $m_1 = m_2 = 2$ g mol^{-1} so $\mu = \frac{2 \times 2}{2+2}$ g mol^{-1} = 1 g mol^{-1}.

Hence, $\frac{\mu_{D_2}}{\mu_{H_2}} = \frac{1}{1/2} = 2$ and $\frac{\mu_{H_2}}{\mu_{D_2}} = \frac{1/2}{1} = 1/2$.

(b) Assuming that H_2 and D_2 have identical force constants, what is the ratio of their vibrational frequencies?

The fundamental frequency is given by:

$$\omega = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

The ratio of the vibrational frequencies of H_2 and D_2 is thus:

$$\frac{\omega_{D_2}}{\omega_{H_2}} = \sqrt{\frac{k_{D_2}}{\mu_{D_2}}} \Big/ \sqrt{\frac{k_{H_2}}{\mu_{H_2}}} = \sqrt{\frac{k_{D_2}\mu_{H_2}}{k_{H_2}\mu_{D_2}}}$$

If $k_{H_2} = k_{D_2}$ and $\frac{\mu_{D_2}}{\mu_{H_2}} = 2$:

$$\frac{\omega_{D_2}}{\omega_{H_2}} = \sqrt{\frac{\mu_{H_2}}{\mu_{D_2}}} = \sqrt{\frac{1}{2}}$$

The vibrational frequency for D_2 is *lower* than that of H_2 and is, approximately, equal to the vibrational frequency for H_2 divided by $\sqrt{2}$.

2. Calculate the reduced mass for HF, HCl, HBr and HI (in atomic mass units).

All the calculations are given to two significant figures. This is sufficient for normal IR spectroscopy. For high resolution work, more accurate values would be used. Note that a separate vibrational frequency could, in principle, by measured for each isotopomer so a separate calculation for each is given below.

For HF, $m_1 = 1$ g mol^{-1} and $m_2 = 19$ g mol^{-1} so $\mu = \frac{1 \times 19}{1+19}$ g mol^{-1} = $\frac{19}{20}$ g mol^{-1}.= 0.95 amu

For $H^{35}Cl$, m_1 = 1 g mol^{-1} and m_2 = 35 g mol^{-1} so $\mu = \dfrac{1 \times 35}{1 + 35}$ g mol^{-1} = $\dfrac{35}{36}$ g mol^{-1}.= 0.97 amu

For $H^{37}Cl$, m_1 = 1 g mol^{-1} and m_2 = 37 g mol^{-1} so $\mu = \dfrac{1 \times 37}{1 + 37}$ g mol^{-1} = $\dfrac{37}{38}$ g mol^{-1}.= 0.97 amu

For $H^{79}Br$, m_1 = 1 g mol^{-1} and m_2 = 37 g mol^{-1} so $\mu = \dfrac{1 \times 79}{1 + 79}$ g mol^{-1} = $\dfrac{79}{80}$ g mol^{-1}.= 0.99 amu

For $H^{81}Br$, m_1 = 1 g mol^{-1} and m_2 = 37 g mol^{-1} so $\mu = \dfrac{1 \times 81}{1 + 81}$ g mol^{-1} = $\dfrac{81}{82}$ g mol^{-1}.= 0.99 amu $^{-1}$

For $H^{127}I$, m_1 = 1 g mol^{-1} and m_2 = 127 g mol^{-1} so $\mu = \dfrac{1 \times 127}{1 + 127}$ g mol^{-1} = $\dfrac{127}{128}$ g mol^{-1}.= 0.99 amu $^{-1}$

3. Using your answer to question 2, what does the reduced mass of a molecule HX tend to as X becomes very heavy?

The reduced mass of HX becomes increasingly close to 1 amu as the mass of X increases. For a molecule AB where the mass of A is much smaller than the mass of B, the reduced mass tends towards the smaller mass:

$$\mu = \frac{m_1 \times m_2}{m_1 + m_2} = \frac{m_1 \times m_2}{m_2} \quad \text{if } m_2 >> m_1\text{. Hence, } \mu \rightarrow \frac{m_1 \times m_2}{m_2} = m_1$$

4. Using your answer to question 3, describe the vibrational motion of the molecule HX as X becomes very heavy.

The molecular vibration approximately corresponds to the lighter end (H) moving and the heavier end (X) being stationary.