

[TP] Red light emitted by H atoms has frequency $\nu_{atom} \sim 5 \times 10^{14}$ Hz. A typical IR frequency is $\nu_{IR} \sim 1 \times 10^{13}$ Hz. This means that, compared to the mass, m_{atom}, of what is moving in response to visible light, the moving mass in IR spectra, m_{IR}, is ...

25% 1. ~ 25 times heavier
25% 2. ~ 250 times heavier
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Lecture 28 CH101 A2 (MWF 11:15 am)

Monday, November 13, 2017

For today ...
- Complete: Using $\Delta_b H$ to *estimate* $\Delta_r H$
- If some substances are not gases, using $\Delta_b H$ works poorly

Begin ch 8: Modeling atoms and their electrons
- Review: What light is and how it interacts with matter
- Natural frequencies of atoms

Next lecture: Light and matter exchange energy smoothly and slowly; Light energy is exchanged in tiny amounts called photons; Electron waves and quantization (de Broglie)

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Using $\Delta_b H$'s to *estimate* $\Delta_r H$

$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(g)$

How much enthalpy change to break reactants apart into atoms?

How much enthalpy change to combine reactant atoms into products?

What is the total enthalpy change?

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Using $\Delta_b H$'s to *estimate* $\Delta_r H$

The key feature of standard bond dissociation energies is that, the enthalpy change of any reaction, $\Delta_r H$, can be estimated using them, as ...

$\Delta_r H$ = Sum[energy spent breaking bonds] –

Sum[energy evolved forming bonds]

= Sum[$\Delta_b H$(reactants)] – Sum[$\Delta_b H$(products)]

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[Quiz] "In my lecture I was told that change in enthalpy is products minus reactants, but my discussion leader told me that it is reactants minus products. I've also looked in another chemistry book and it say products minus reactants. Which is right?"

25% 1. products minus reactants
25% 2. reactants minus products
25% 3. both
25% 4. neither

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If some substances are not gases, using $\Delta_b H$ works poorly

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$\Delta_f H°$ versus $\Delta_b H$ to compute $\Delta_r H$

$$C_2H_5OH(g) + 3\ O_2(g) \rightarrow 2\ CO_2(g) + 3\ H_2O(g)$$

Using standard enthalpies of formation:

$$\Delta_r H = +\ 2\ \Delta H_f(CO_2, g) + 3\ \Delta H_f(H_2O, g) - \Delta H_f(C_2H_5OH, g) = -\ 1{,}277.38\ \text{kJ}$$

Using bond enthalpies:

$$\Delta_r H = +\ \Delta H_{break}(C_2H_5OH) + 3\ \Delta H_{break}(O_2) - 2\ \Delta H_{make}(CO_2) - 3\ \Delta H_{make}(H_2O) = -\ 1{,}232\ \text{kJ}$$

Good agreement!

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$\Delta_f H°$ versus $\Delta_b H$ to compute $\Delta_r H$

$$C(s, gr) + 2\ H_2O(g) \rightarrow CH_4(g) + O_2(g)$$

Using standard enthalpies of formation:

$$\Delta_r H = +\ \Delta H_f(CH_4, g) - 2\ \Delta H_f(H_2O, g)$$
$$= -\ 74.81 - 2(-\ 241.82) = +\ 408.83\ \text{kJ}\ (\textit{actual})$$

Using bond enthalpies:

$$\Delta_r H = +\ 2\ \Delta H_{break}(H_2O) - \Delta H_{make}(CH_4) - \Delta H_{make}(O_2)$$
$$= +\ 4\ (\text{O-H}) - 4(\text{C-H}) - (\text{O=O})$$
$$= 4(460) - 4(414) - 498.7 = -\ 315\ \text{kJ}\ (\textit{approximate})$$

Big error!

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$\Delta_f H°$'s versus $\Delta_b H$'s to compute $\Delta_r H$

$$C(s, gr) + 2\,H_2O(g) \rightarrow CH_4(g) + O_2(g)$$

Using standard enthalpies of formation:

$$\Delta_r H = +\,\Delta H_f(CH_4, g) - 2\,\Delta H_f(H_2O, g)$$
$$= -74.81 - 2(-241.82) = +\,408.83 \text{ kJ } (actual)$$

Using bond enthalpies:

$$C(s, gr) \rightarrow C(g),\ \Delta H_f(C, g)$$
$$\Delta_r H = \Delta H_f(C, g) + 2\,\Delta H_{break}(H_2O) - \Delta H_{make}(CH_4) - \Delta H_{make}(O_2)$$
$$= \Delta H_f(C, g) + 4\,(O\text{-}H) - 4(C\text{-}H) - (O{=}O)$$
$$= 716.7 + 4(460) - 4(414) - 498.7 = +\,402 \text{ kJ } (approximate)$$

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Much better!

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Review: What light is and how it interacts with matter

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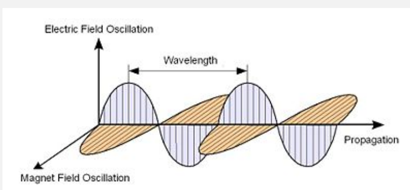
Matter experiences light as an oscillating electric field



The electric field strength changes direction at frequency ν_{light}.

(The effect of the magnetic field is relatively negligible.)

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The changing electric field of light tugs on matter …

Matter can respond to tugs only at “natural” frequencies of “motion” in matter

$$\nu_{light} = \nu_{matter}$$

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Matter responds only at its "natural" frequencies

C-O stretch ~1000 $\text{cm}^{-1} = 3 \times 10^{13}$/s

ν_{stretch} = relative motion of atoms

$\nu_{\text{light}} = \nu_{\text{stretch}}$

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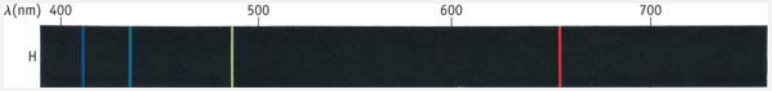
What are natural frequencies of atoms?

Here is the H atom emission spectrum.



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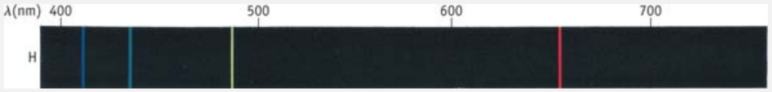

There are four "lines", at 410 nm, 434 nm, 486 nm, and 656 nm.

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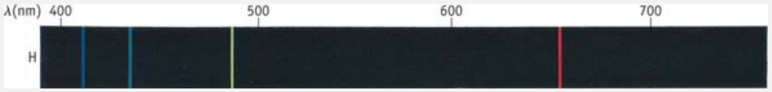

Since light interacts with matter when $\nu_{\text{light}} = \nu_{\text{matter}}$, these lines mean …

there is motion in the atom

at the frequencies, ν_{atom}, corresponding to these lines.

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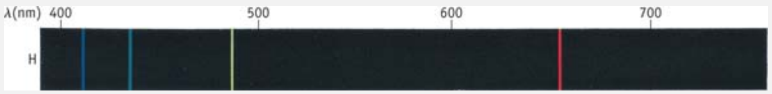
What are natural frequencies of atoms?

Here is the H atom emission spectrum.



What is the frequency of motion in the H atom corresponding to the 656 nm line?

$$\nu_{\text{atom}} = \frac{c}{\lambda_{\text{atom}}} = \frac{2.998 \times 10^{8}\,\text{m/s}}{656\ \text{nm}} = 4.57 \times 10^{14}\text{s} \sim 5 \times 10^{14}\text{s}$$

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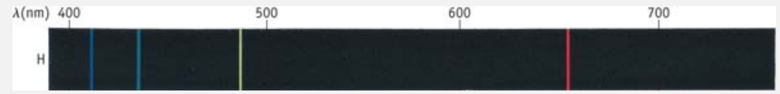
What are natural frequencies of atoms?

Here is the H atom emission spectrum.



The red light emitted has frequency $\nu_{\text{atom}} \sim 5 \times 10^{14}$ Hz.

For IR, at typical frequency due to the oscillation of light atoms is $\nu_{\text{IR}} \sim 1 \times 10^{13}$ Hz.

Estimate the ratio of the mass of what is moving in H atom, m_{atom}, relative to the mass moving at $\sim 1 \times 10^{13}$ Hz, m_{IR}.

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What are natural frequencies of atoms?

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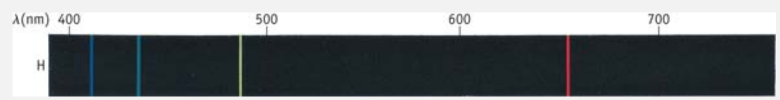

Estimate the ratio of the mass of what is moving in H atom, m_{atom}, relative to the mass moving at $\sim 1 \times 10^{13}$ Hz, m_{IR}.

$$\nu_{\text{atom}}/\nu_{\text{IR}} \sim 50 = \sqrt{\frac{m_{\text{IR}}}{m_{\text{atom}}}}$$

$m_{\text{IR}}/m_{\text{atom}} \sim 50^2$ so m_{IR} is ~ 2500 times heavier than m_{atom}.

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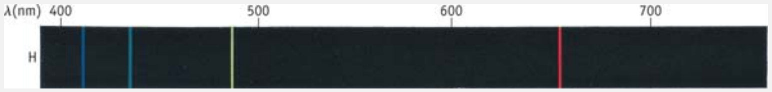
What are natural frequencies of atoms?

Here is the H atom emission spectrum.



$m_{\text{IR}}/m_{\text{atom}} \sim 50^2$ so m_{IR} is ~ 2500 times heavier than m_{atom}.

So, what is it that is moving in the atom in response to visible light that is so much lighter that the atoms themselves moving in response to IR light?

Motion of electron clouds accounts for how atoms interact with light:

$$\nu_{\text{light}} = \nu_{\text{cloud}}$$

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