ChemE 2200 – Applied Quantum Chemistry Lecture 4

Today:

The Interaction of Electromagnetic Radiation with Matter:

Molecular Spectroscopy Overview

Rotational Transitions and Microwave Spectroscopy

Defining Question:

What molecular property is required for a diatomic molecule to absorb/emit microwave radiation?

Reading for Today's Lecture:

McQuarrie & Simon, 5.8, 5.9, 13.1, 13.2, 13.11, and 13.12.

Reading for Quantum Lecture 5:

McQuarrie & Simon, 5.1 – 5.7.

Weekly Quizzes

Conducted first 10-15 minutes of Calculation Session.

Based on homework assigned previous Wednesday.

Will strive for a mean of 9-10 out of 10
if you learned from working the homework.

You may use your handwritten reference sheet
you are preparing for prelims.

No make-up quizzes. Two lowest scores will be dropped.

TA Office Hours

Sunday and Tuesday (not Wednesday) evenings.
7:00-9:00 p.m., 128 Olin Hall

TMD Office Hours

Monday noon – 2:00 p.m., 344A Olin Hall

Recall – Homework solutions are posted when the homework is assigned.

The Interaction of Electromagnetic Radiation with Matter

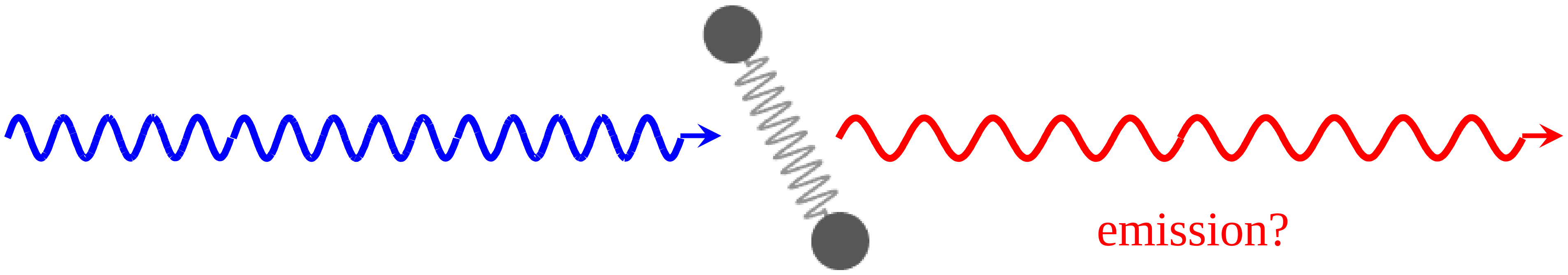
Why is CO_2 a greenhouse gas? Why are O_2 and N_2 not greenhouse gases?

How does ozone (O_3) screen ultraviolet radiation? And O_2 and N_2 do not?

Can electromagnetic radiation from a smart phone cause cancer?
from power lines and transformers?
from blacklights?

What are the consequences of absorbing 1 kJ of microwaves?
1 kJ of infrared?
1 kJ of visible light?
1 kJ of ultraviolet radiation?
1 kJ of x-ray radiation?

The Interaction of Electromagnetic Radiation with Matter



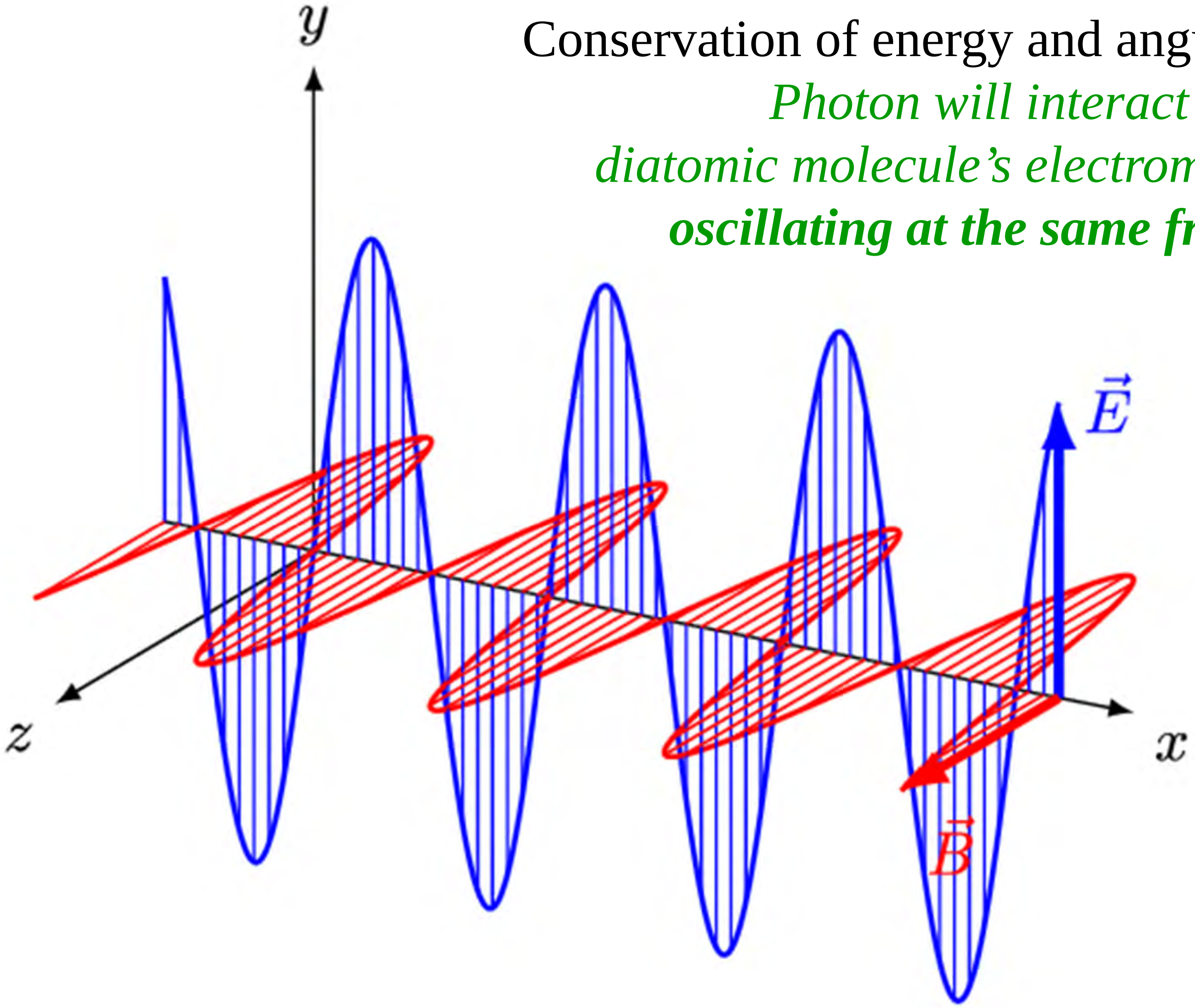
Absorption and/or emission must conserve energy.

Absorption and/or emission must conserve angular momentum.

The Interaction of Electromagnetic Radiation with Matter

A photon is an oscillating electromagnetic field.

Conservation of energy and angular momentum:
Photon will interact with
diatomic molecule's electromagnetic field
***oscillating at the same frequency*.**



A diatomic electric dipole
is an oscillating
electromagnetic field.

velocity = c = (wavelength) × (frequency)

frequency = c/wavelength

Image from commons.wikimedia.org/wiki/File:EM-Wave.gif

Image from downloadhdwallpapers.in/
molecular-vibration-representation/

The Interaction of Electromagnetic Radiation with Matter

Applications:

Treat the material:	(selectively) heat molecules.	Medical Treatment
	(selectively) ionize molecules	Purification
	(selectively) break bonds	Strategic Chemical Reactions

Analyze the material: identify chemical composition
measure concentration
measure temperature
measure pressure

Molecular Spectroscopy

Phenomenon	Photon Energy	Effect
rotational transitions	$10^{-4} - 10^{-3}$ eV	heat
vibrational transitions	$10^{-2} - 1$ eV	light
electronic transitions	$1 - 100$ eV	chemical reaction

Molecular Spectroscopy

Calculating the photon spectrum of a molecular transition:

1. Describe the molecule with quantum mechanics.

   Solve $H\Psi = E\Psi$ for Ψ. Match boundary conditions. Normalize.

2. Calculate the molecular energy levels $E_1, E_2, \ldots$

3. Determine the selection rules for photon-induced transitions.

   Conservation of energy: $E_{\text{photon}} = E_{\text{final}} - E_{\text{initial}}$

   Conservation of angular momentum: $J_{\text{photon}} = J_{\text{final}} - J_{\text{initial}}$

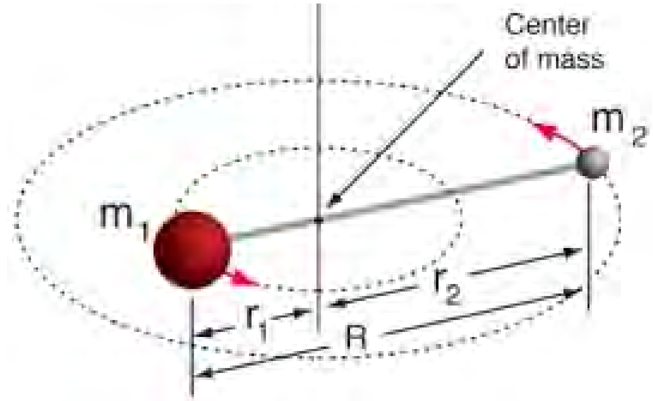
   Initial state occupied?

   Final state vacant?

4. Determine the spectral intensities (peak heights in the photon spectrum).

Rotational Transitions in Diatomic Molecules

Molecule rotates around center of mass



You already derived the rotational wavefunctions when you analyzed the hydrogen atom.

$H\Psi = E\Psi$ separates into a radial term and an angular term: $\Psi(r,\theta,\varphi) = \mathrm{R}(r)\mathrm{Y}(\theta,\varphi)$

For a fixed *r*, the wavefunctions are the spherical harmonics.

$\Psi = \mathrm{Y}_{J,mJ}(\theta,\varphi)$ quantum numbers are J and m_J (analogous to ℓ and m_ℓ for the H atom.)

$J = 0, 1, 2, \ldots \quad m_\mathrm{J} = 0, \pm1, \pm2, \ldots, \pm J$

total angular momentum $= |J| = [J(J+1)]^{1/2}\hbar$

angular momentum projection onto rotation axis (x or y) $= J_x = m_\mathrm{J}\hbar$

$$E_\mathrm{J} = \frac{|J|^2}{2I} = \frac{J(J+1)\hbar^2}{2I}$$

$$\text{moment of inertia} = I = m_1 r_1^2 + m_2 r_2^2 = \frac{m_1 m_2}{m_1+m_2}R^2 = \mu R^2$$

$$\text{reduced mass} = \mu = \frac{m_1 m_2}{m_1+m_2}$$

Diatomic image from hyperphysics.phy-astr.gsu.edu

Photon Wavenumbers

Rotational energy levels are extremely small numbers in units of Joules. $E_J \approx 10^{-26}\ \mathrm{J}$

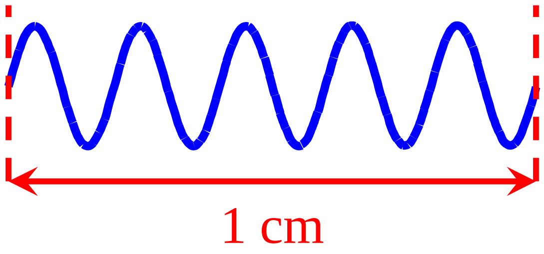
Tradition dictates that rotational energies are reported in units of wavenumbers.

Wavenumber is the *number* of cycles (*waves*) per unit length, typically a cm.

$$\text{photon wavenumber} = \tilde{\nu} = \frac{1}{\text{wavelength}} = \frac{1}{\lambda}$$

$$\tilde{\nu} = \frac{\text{frequency}}{c} = \frac{\nu}{c}$$

Typical units for wavenumber are cm^{-1}.



$$\tilde{\nu} = 5\,\mathrm{cm}^{-1}$$

Rotational Energy Levels

$$E = hv = hc\tilde{v}$$

$$\tilde{v}_J = \frac{E_J}{hc} = \frac{J(J+1)\hbar^2}{hc2I} = \frac{J(J+1)\hbar^2}{(2\pi\hbar)c2I} = \frac{\hbar}{4\pi cI}J(J+1)$$

$$\text{Define } B \equiv \text{rotational constant} = \frac{\hbar}{4\pi c I}$$

moment of inertia depends on molecule.

$$\boxed{\tilde{v}_J = \frac{E_J}{hc} = BJ(J+1)}$$

Note: the rotational 'constant' is not constant.

$$\boxed{I = \frac{m_1 m_2}{m_1 + m_2}R^2}$$

	diatomic	R	B	
smallest I →	$^1H_2$	0.74 Å	60.85 cm^{-1}	← largest B
	$^2H_2$	0.74 Å	30.43 cm^{-1}	← mass doubles, B halves
	$^1H^{19}F$	0.92 Å	20.96 cm^{-1}	
	$^1H^{127}I$	1.62 Å	6.52 cm^{-1}	H spins around stationary I
	$^{19}F_2$	1.41 Å	0.890 cm^{-1}	
	$^{127}I_2$	2.67 Å	0.0373 cm^{-1}	$^1H_2$/1600

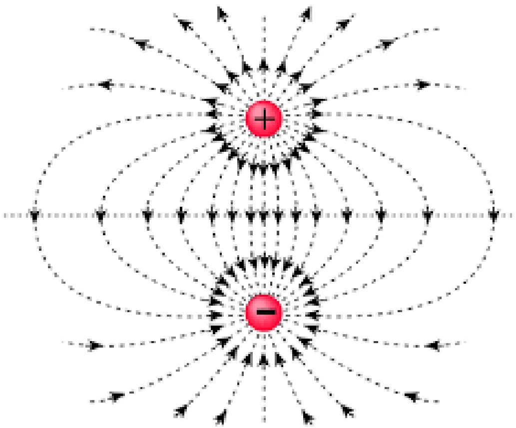
see Table 13.2, p. 499
McQuarrie & Simon

The Photon Spectrum of Rotational Transitions

1. Describe the molecule with quantum mechanics. ✓
2. Calculate molecular energy levels E_1, E_2, … ✓
3. Determine selection rules for photon-induced transitions.

Photon will interact with diatomic's electromagnetic field oscillating at the same frequency.

For molecular rotation to create
an oscillating electromagnetic field,
the molecule must have a permanent dipole.



N≡N	14 electrons	symmetric molecule	no electric dipole
C≡O	14 electrons	oxygen has stronger attraction for e^-	electric dipole
F–F	18 electrons	symmetric molecule	no electric dipole
H–Cl	18 electrons	chlorine has stronger attraction for e^-	electric dipole

A diatomic molecule must be asymmetric for a photon-induced rotational transition.

Selection Rules for Spherical Harmonics

Atoms	Diatomic Molecules
electronic transition (*e.g.* 1s → 2p)	rotational transition (*e.g.* $J = 0 \rightarrow J = ?$)
$\Delta\ell = \pm 1$	$\Delta J = \pm 1$
and $\Delta m_\ell = 0, \pm 1$	and $\Delta m_J = 0, \pm 1$
$\Delta E \sim 10{,}000\ \text{cm}^{-1}$	$\Delta E \sim 10\ \text{cm}^{-1}$

Why a factor of ~1000 difference in energy?

mass of nucleus ≈ 1800 × mass of electron

nucleus + electron moment of inertia ≈ (diatomic moment of inertia)/1800 for H_2

photon energy for photon absorption. $J \rightarrow J+1$

$$E_{\text{photon}} = E_{J+1} - E_J$$

$$hc\tilde{\nu}_{\text{photon}} = hc\tilde{\nu}_{J+1} - hc\tilde{\nu}_J$$

$$\tilde{\nu}_{\text{photon}} = \tilde{\nu}_{J+1} - \tilde{\nu}_J$$

The Photon Spectrum of Rotational Transitions

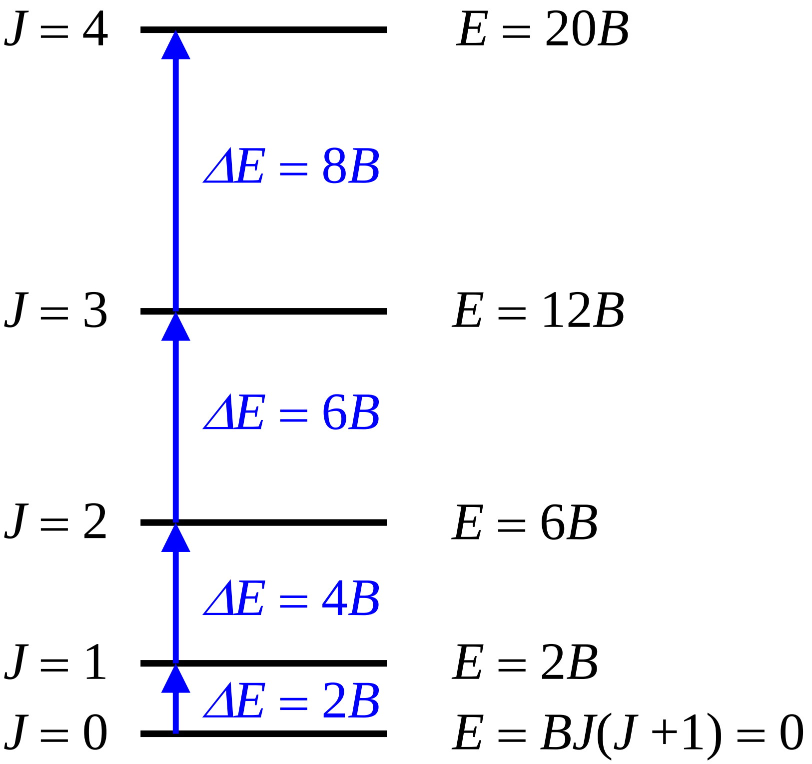
$$\tilde{\nu}_{\text{photon}} = \tilde{\nu}_{J+1} - \tilde{\nu}_J = B(J+1)(J+2) - BJ(J+1)$$

$$= B(J^2+3J+2-(J^2+J))$$

$$= B(2J+2)$$

$$\boxed{\tilde{\nu}_{\text{photon}} = 2B(J+1)} \qquad \Delta J = \pm 1$$

Calculate the first few peaks in the photon spectrum.



$J = 4$ $E = 20B$

$\Delta E = 8B$

$J = 3$ $E = 12B$

$\Delta E = 6B$

$J = 2$ $E = 6B$

$\Delta E = 4B$

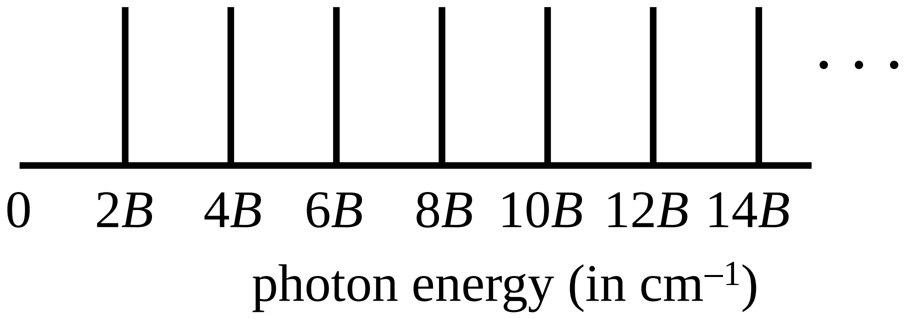
$J = 1$ $E = 2B$

$\Delta E = 2B$

$J = 0$ $E = BJ(J+1) = 0$

initial level	final level	$\tilde{\nu}_{\text{photon}}$
$J = 0$	$J = 1$	$2B$
1	2	$4B$
2	3	$6B$
3	4	$8B$

photon spectrum:



The Photon Spectrum of Rotational Transitions

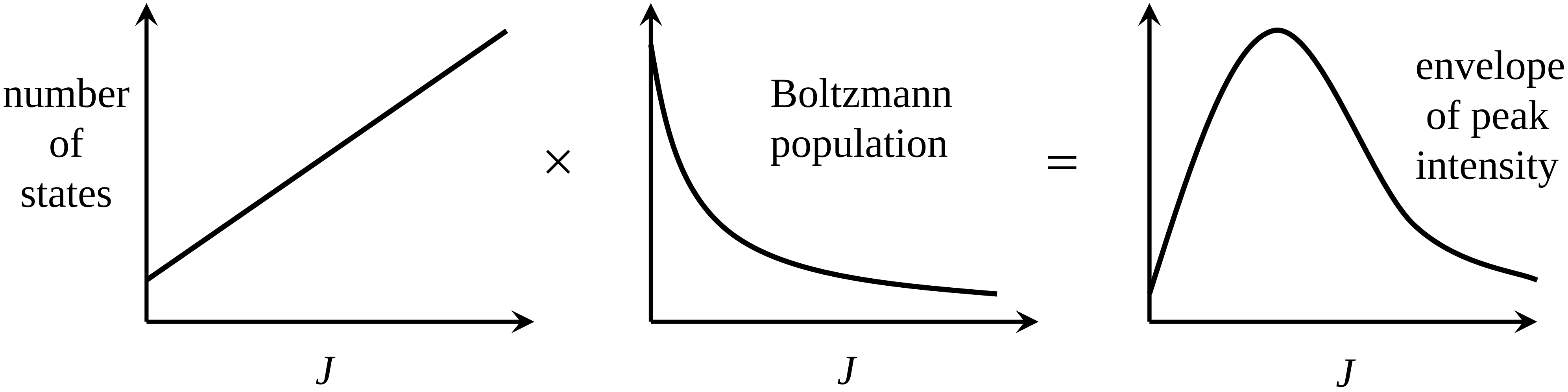
Peak intensities in the photon spectrum.

peak intensity ∝ (number of states at initial energy) × (Boltzmann population at initial energy)

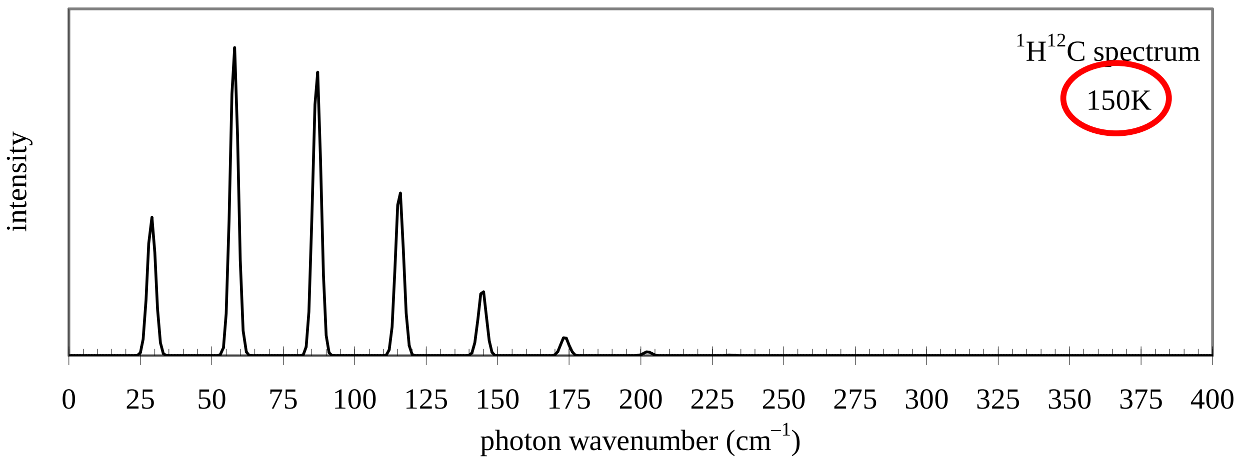
number of states:

J	$m_J = 0, \pm 1, \ldots \pm J$	number of states
0	0	1
1	+1, 0, –1	3
2	+2, +1, 0, –1, –2	5
J	$+J, \ldots 0 \ldots, -J$	$2J+1$

$$\text{Boltzmann population} \propto e^{-E/kT} = \exp\left[\frac{-BJ(J+1)hc}{kT}\right]$$

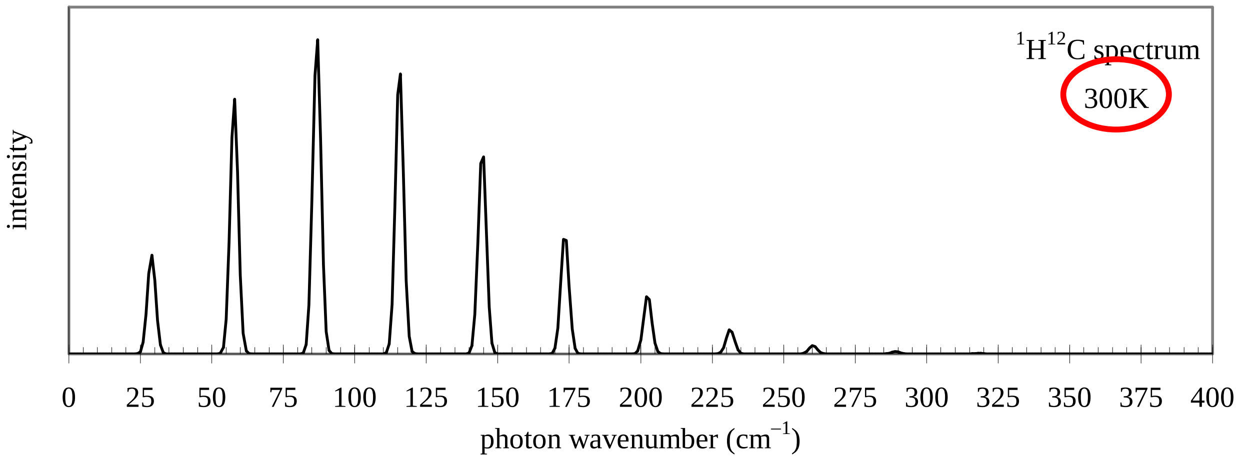


Rotational Spectra of $^{1}H^{12}C$

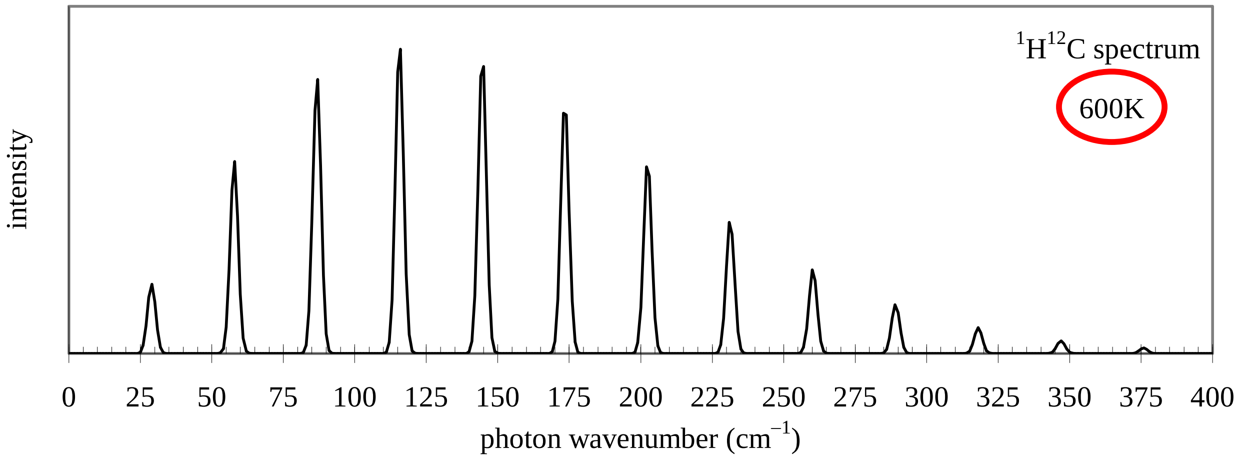


$2B = 28.91\ cm^{-1}$

Rotational transitions are in the *microwave* portion of the electromagnetic spectrum.



Peak intensity envelope increases as temperature increases.



Peak linewidth is also determined by temperature, as well as pressure.

But beyond the scope of ChemE 2200

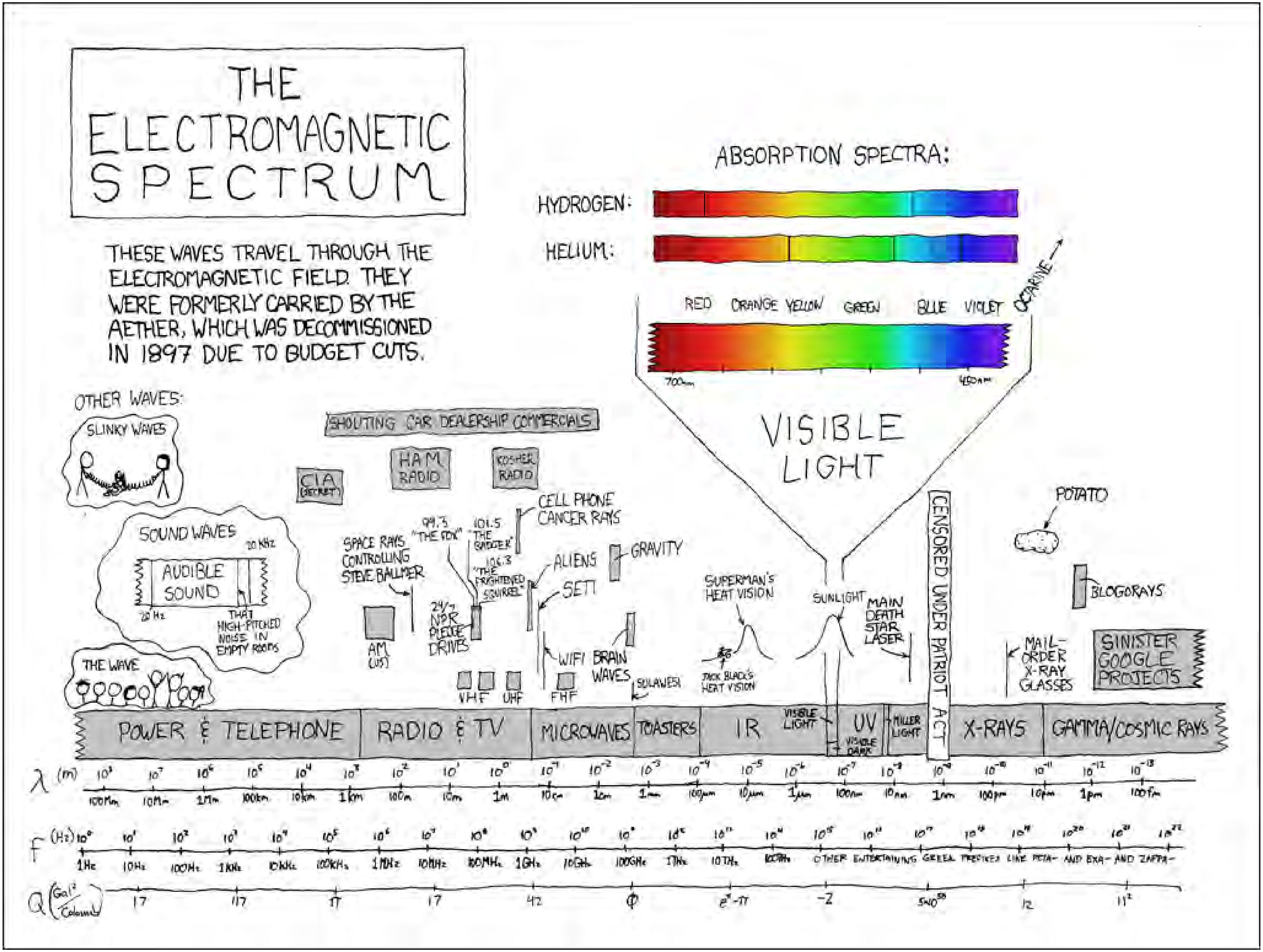
Microwave Photons are Low Energy

The Electromagnetic Spectrum

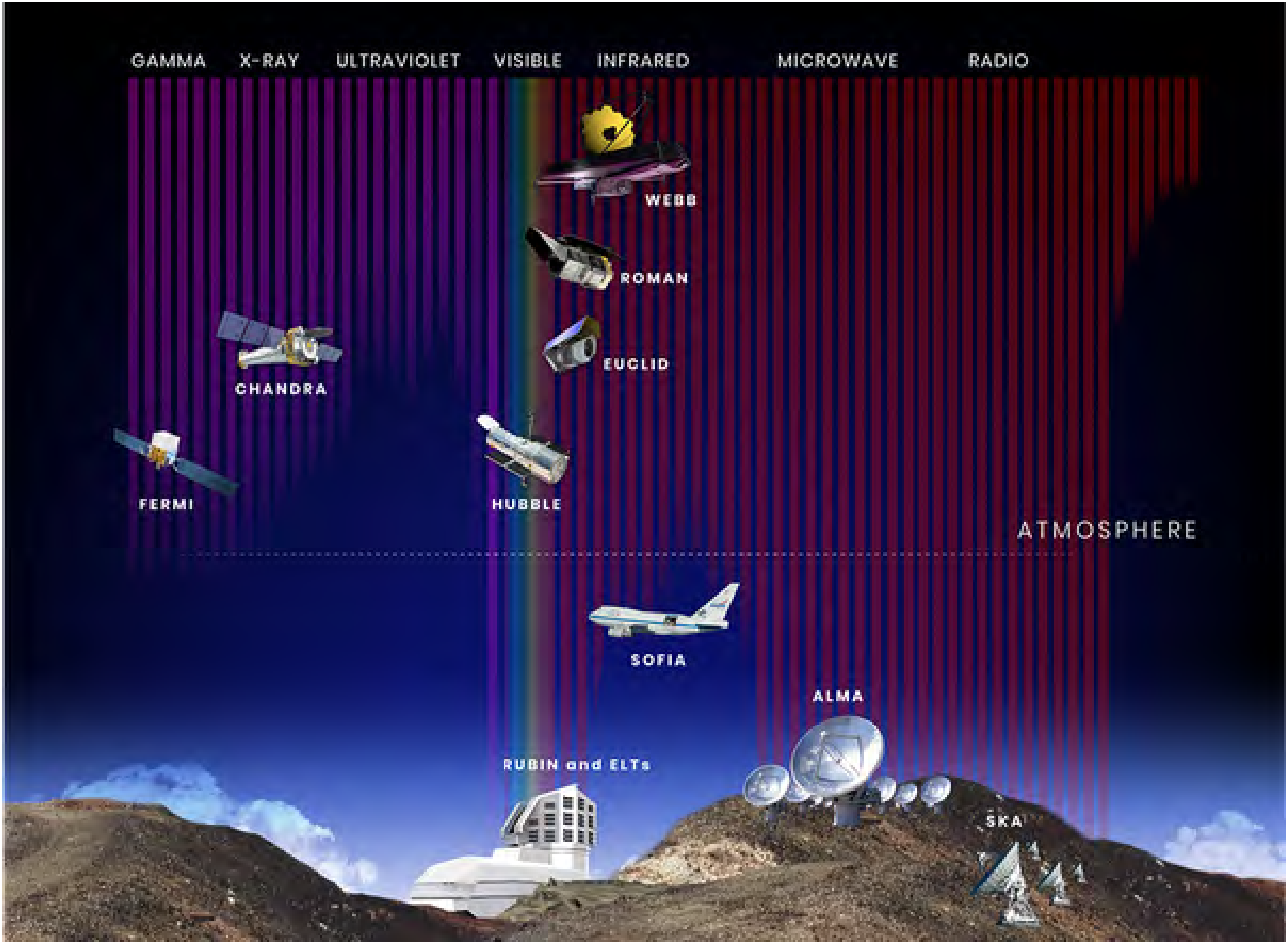
frequency, ν	band		photon energy = hν		wavelength	wavenumber	source
(cycles/sec)	name	phenomenon	eV	kJ/mol	$\lambda = c/\nu$	$\tilde{\nu} = 1/\lambda$	temperature*
10^{23}	cosmic rays	supernovae	4×10^{8}		3 fm		10^{12} K
10^{22}	gamma rays	nuclear decay	4×10^{7}		30 fm		10^{11} K
10^{21}			4×10^{6}		0.3 pm		10^{10} K
10^{20}	x rays	ejection of core electrons	4×10^{5}		3 pm		10^{9} K
10^{19}			4×10^{4}		30 pm		10^{8} K
10^{18}			4×10^{3}		0.3 nm		10^{7} K
10^{17}	ultraviolet	excitation of valence electrons	400	40,000	3 nm		10^{6} K
10^{16}			40	4000	30 nm		10^{5} K
10^{15}	visible light		4	400	0.3 μm		10^{4} K
10^{14}	infrared	molecular vibrational levels	0.4	40	3 μm	3000 cm^{-1}	10^{3} K
10^{13}			0.04	4	30 μm	300 cm^{-1}	100 K
10^{12}				0.4	0.3 mm	30 cm^{-1}	10 K
10^{11}	microwaves	molecular rotational levels	0.0004 eV	0.04	3 mm	3 cm^{-1}	1 K
10^{10}					3 cm		0.1 K
10^{9}					30 cm		10 mK
10^{8}	radio waves	TV, FM radio, computer chips, shortwave radio, AM radio			3 m		1 mK
10^{7}					30 m		
10^{6}					300 m		
10^{5}					3 km		
10^{4}	power	ac electricity			30 km		
10^{3}					300 km		
100					3×10^{3} km		
10					3×10^{4} km		
1					3×10^{5} km		

1 eV = 1.60×10^{-19} J = 8066 cm^{-1}

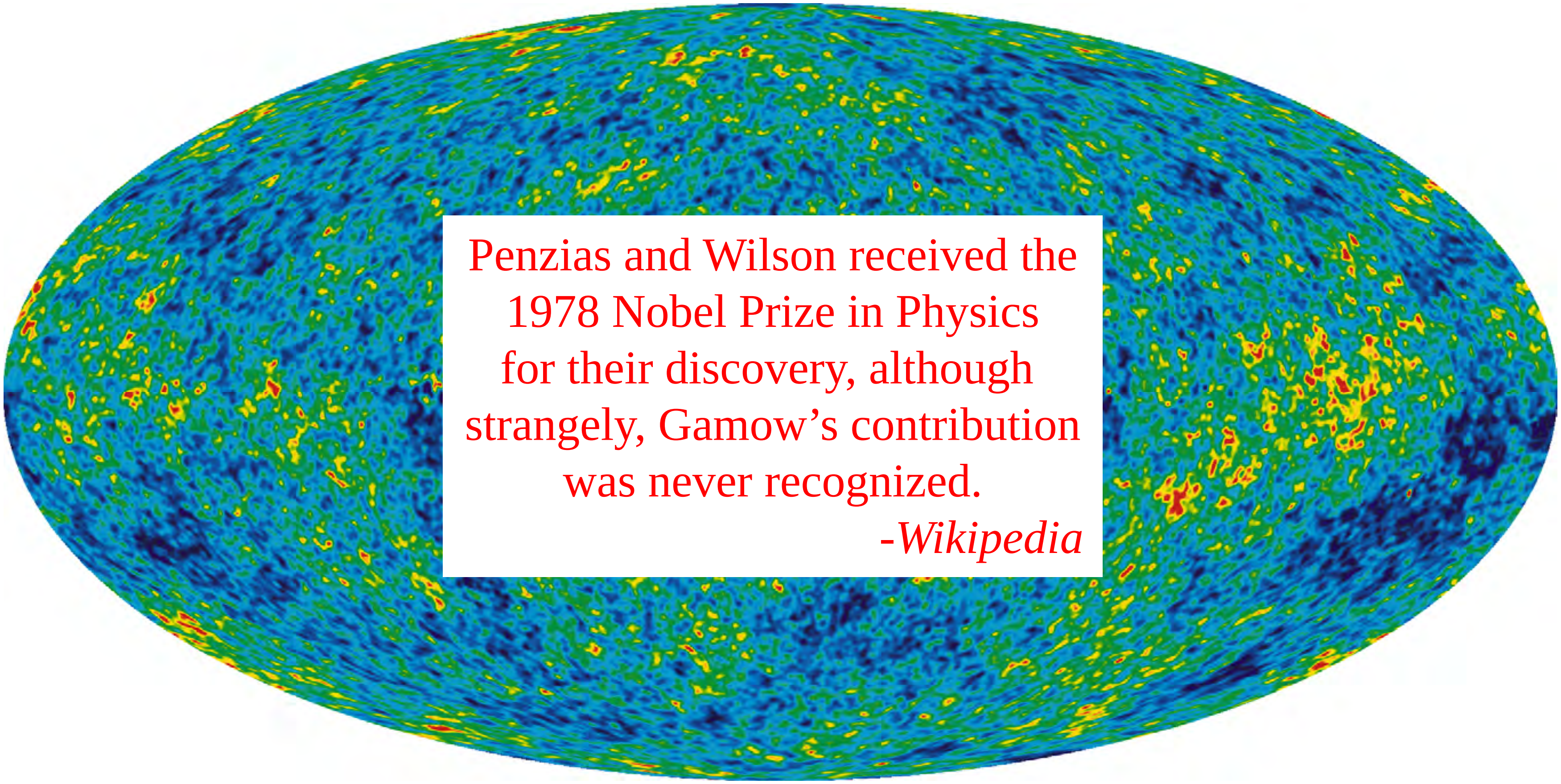
*temperature of a body that will emit photons chiefly at this energy. The maximum of the Planck distribution, $T = h\nu/(5k)$



Randal Munroe, www.xkcd.com/273/ June 6, 2007 (edited to a PG version).


GAMMA
X-RAY
ULTRAVIOLET
VISIBLE
INFRARED
MICROWAVE
RADIO
WEBB
ROMAN
CHANDRA
EUCLID
FERMI
HUBBLE
ATMOSPHERE
SOFIA
ALMA
RUBIN and ELTs
SKA

The Cosmic Microwave Background



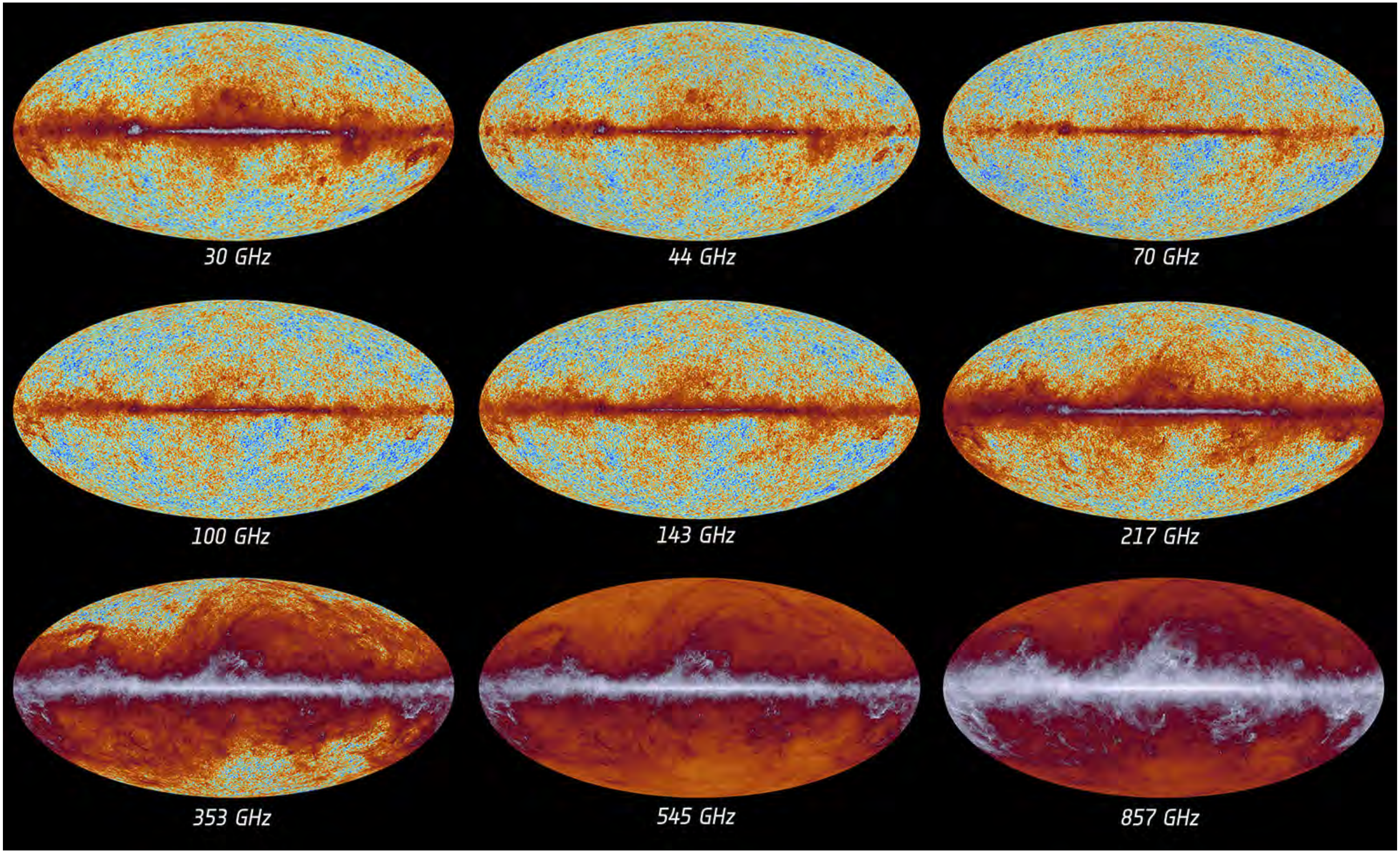
Penzias and Wilson received the 1978 Nobel Prize in Physics for their discovery, although strangely, Gamow's contribution was never recognized.

-Wikipedia

In 1948 the Ukrainian-American physicist George Gamov realized that the huge heat from a hot Big Bang could not dissipate in the same way as the heat from a regular explosion and therefore it must still be around today.

In 1965, Arno Penzias and Robert Wilson, two young employees of Bell Laboratories, discovered, although totally by accident, exactly that. The mysterious microwave background they detected with their microwave antenna seemed to be coming equally from every direction in the sky, and eventually they realized that this microwave radiation (which has a temperature of about 3K) must indeed be the "afterglow" of the Big Bang.

The Cosmic Microwave Background



How did Penzias and Wilson know the source temperature was 3K?

Measure intensities at different wavelengths!