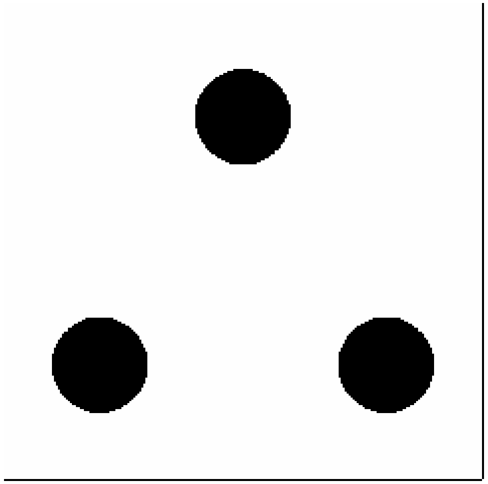
Laboratory spectroscopy of H_3^+



Ben McCall
Oka Ion Factory™
University of Chicago

Motivations

- Astronomical
  - obtain frequencies for detection & use as probe
- Quantum Mechanical
  - study structure of this fundamental ion
  - refine theoretical calculations of polyatomics

Formation of H_3^+

H_2 Proton Affinity:
~ 4.4 eV
~ 100 kcal/mol
~ $D(H_2)$

H_2 — e^- impact (laboratory plasma)

$$H_2^+ + H_2 \rightarrow H_3^+ + H$$

H_2 — cosmic ray (interstellar medium)

Rate constant: $k \sim 2 \times 10^{-9}\ cm^3\ s^{-1}$

Exothermicity: $\Delta H \sim 1.7$ eV

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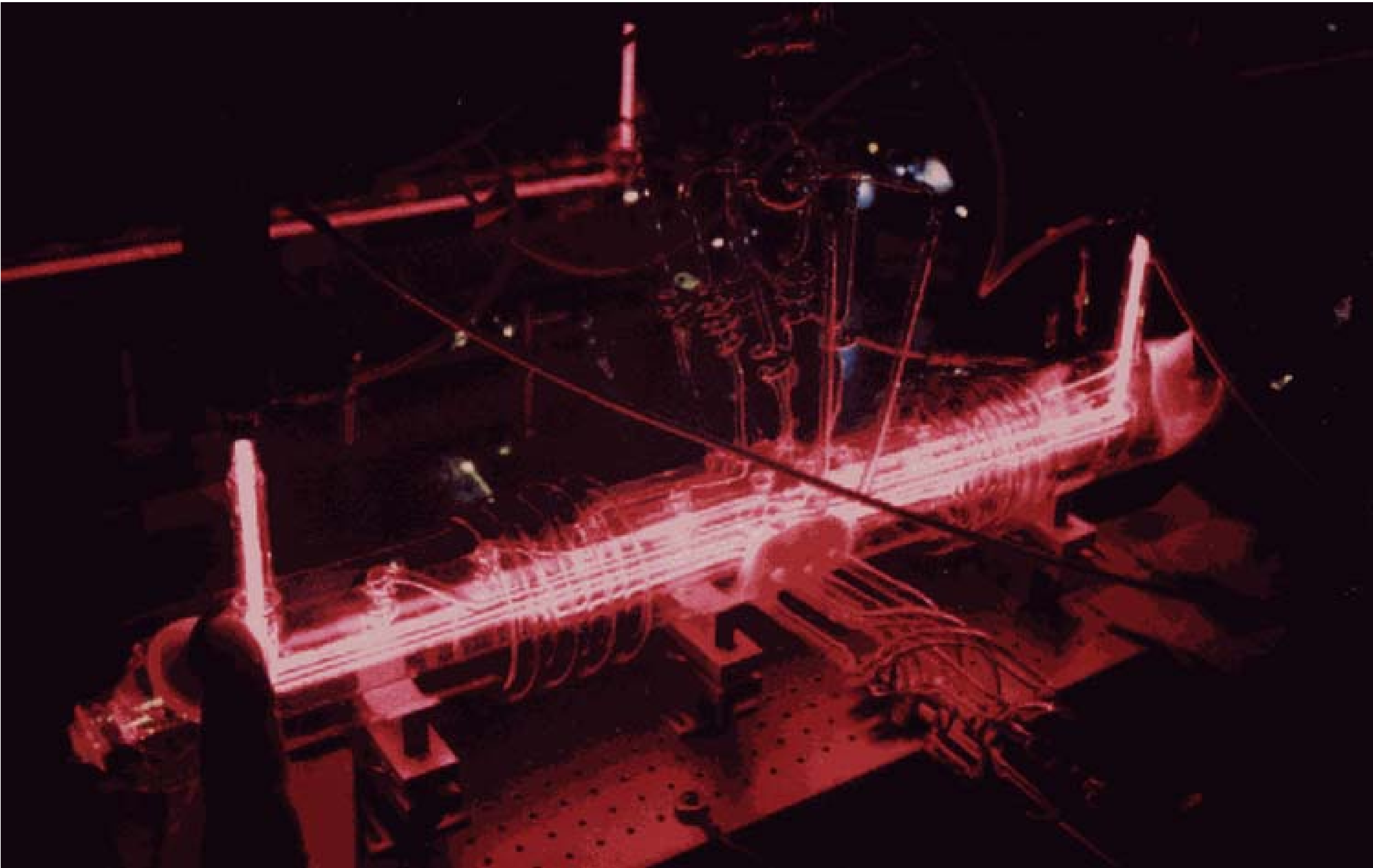
Laboratory Plasma



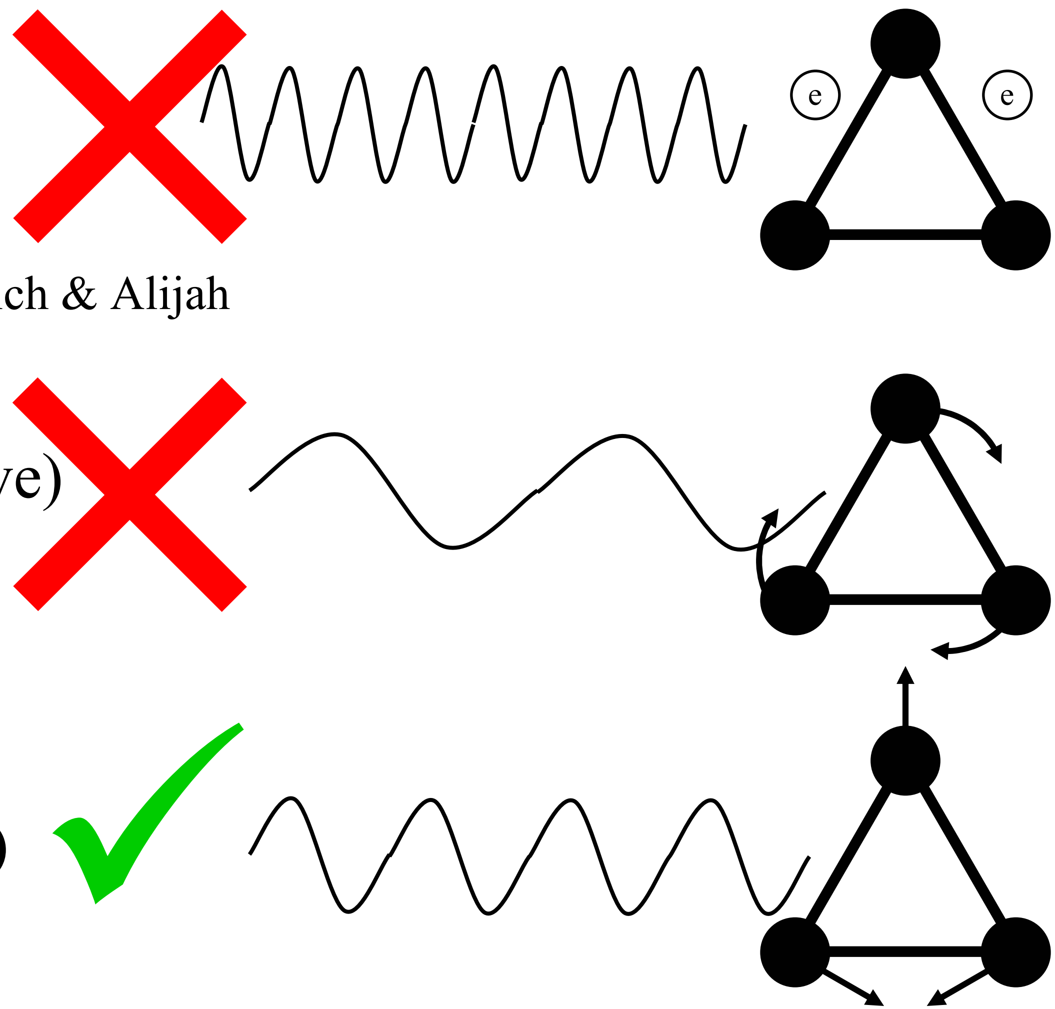
Types of Molecular Spectroscopy

Electronic (visible)

Poster: Friedrich & Alijah

Rotational (microwave)

Vibrational (infrared)



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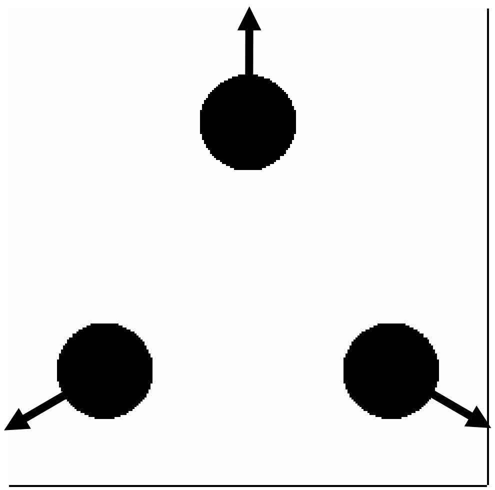
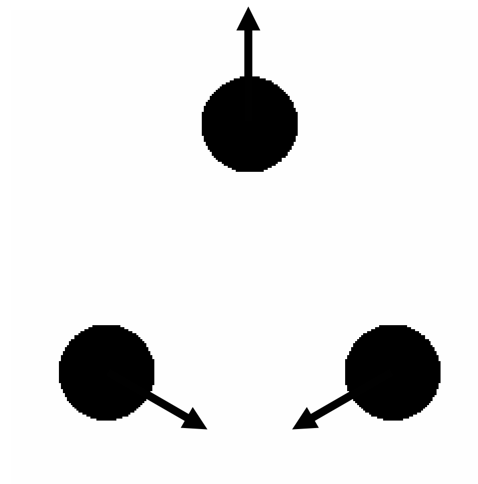
Vibrational Modes of H_3^+

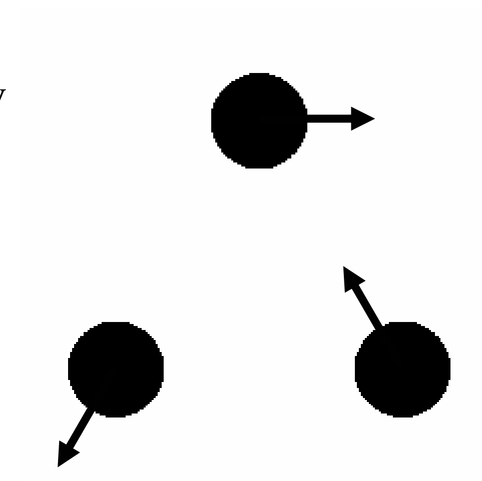
ν_1



ν_{2x}



ν_{2y}



Infrared inactive

Infrared active

Degenerate
⇓
any linear combination

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Vibrational Modes of H_3^+

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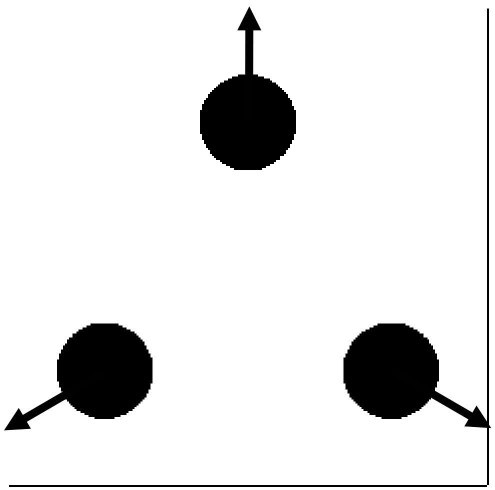

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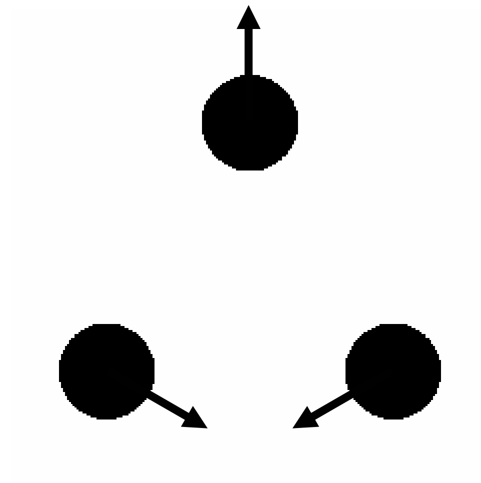

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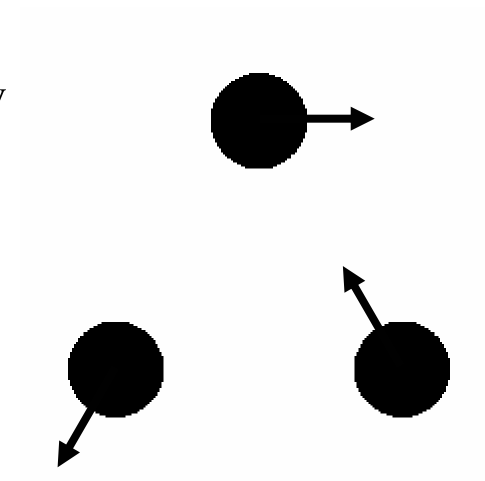
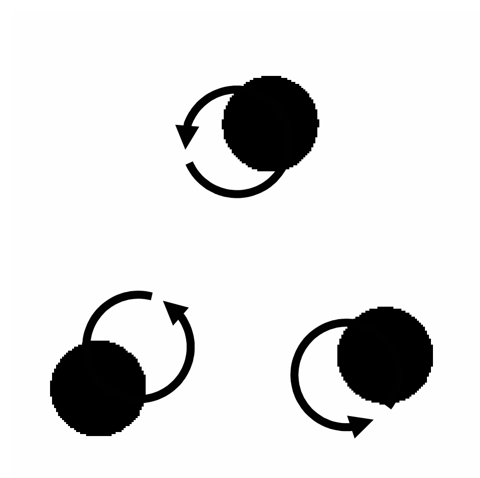


ν_{2+}



vibrational angular momentum

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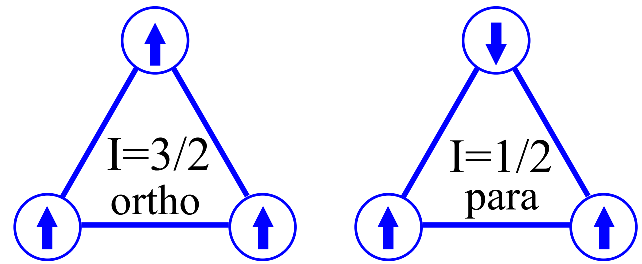
Quantum Numbers for H_3^+



- Angular momentum
  - I — nuclear spin
  - J — nuclear motion
    - k = projection of J ; K = |k|
  - l_2 — vibration
- "l-resonance": states with same $|k-l_2|$ mixed
  - $G \equiv |k-l_2|$ — rotational part of J
- Symmetry requirements
  - $G=3n \leftrightarrow$ ortho, $G\neq 3n \leftrightarrow$ para
  - Pauli: certain levels forbidden (J=even, G=0)

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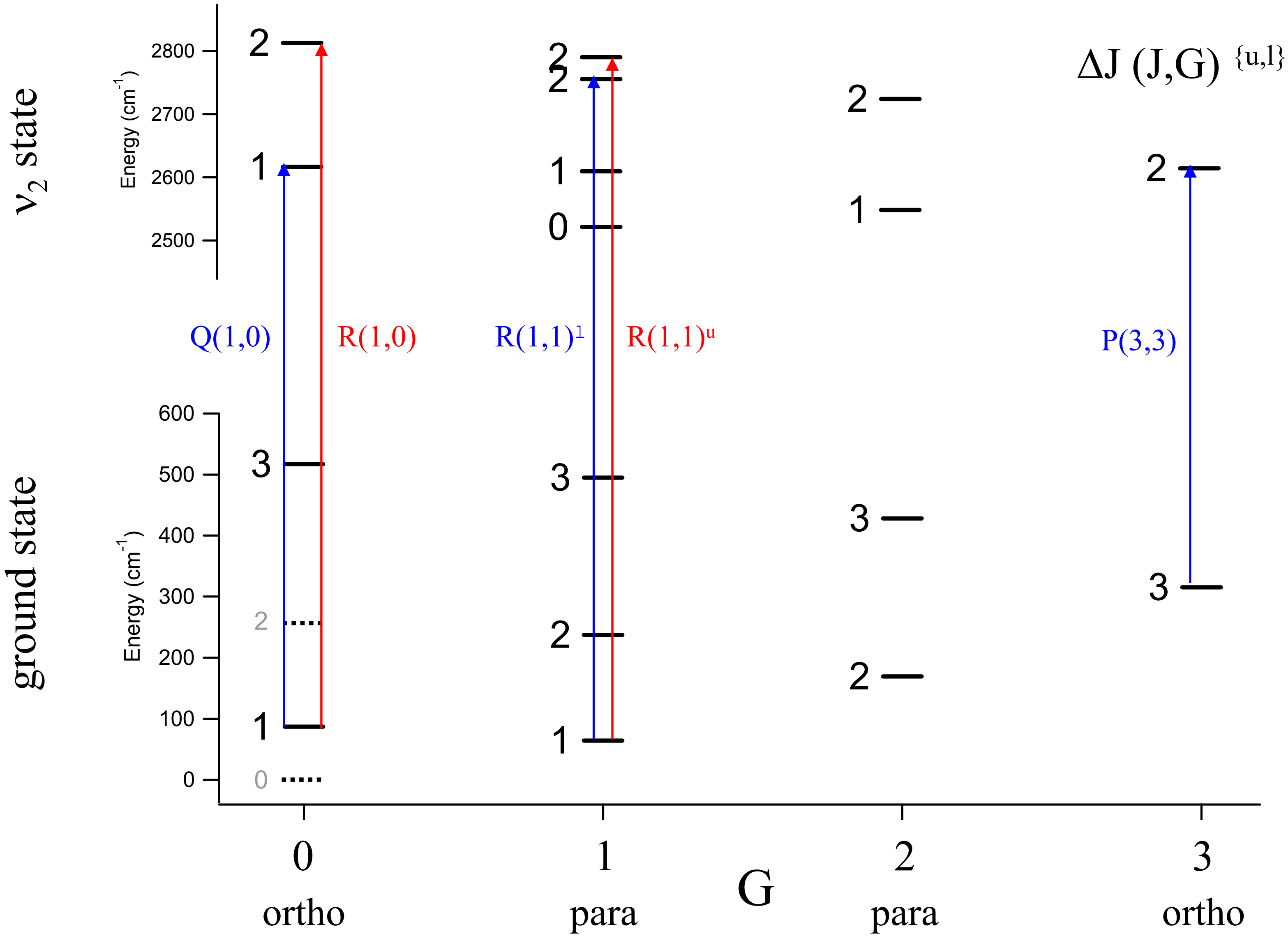
The $\nu_2 \leftarrow 0$ fundamental band



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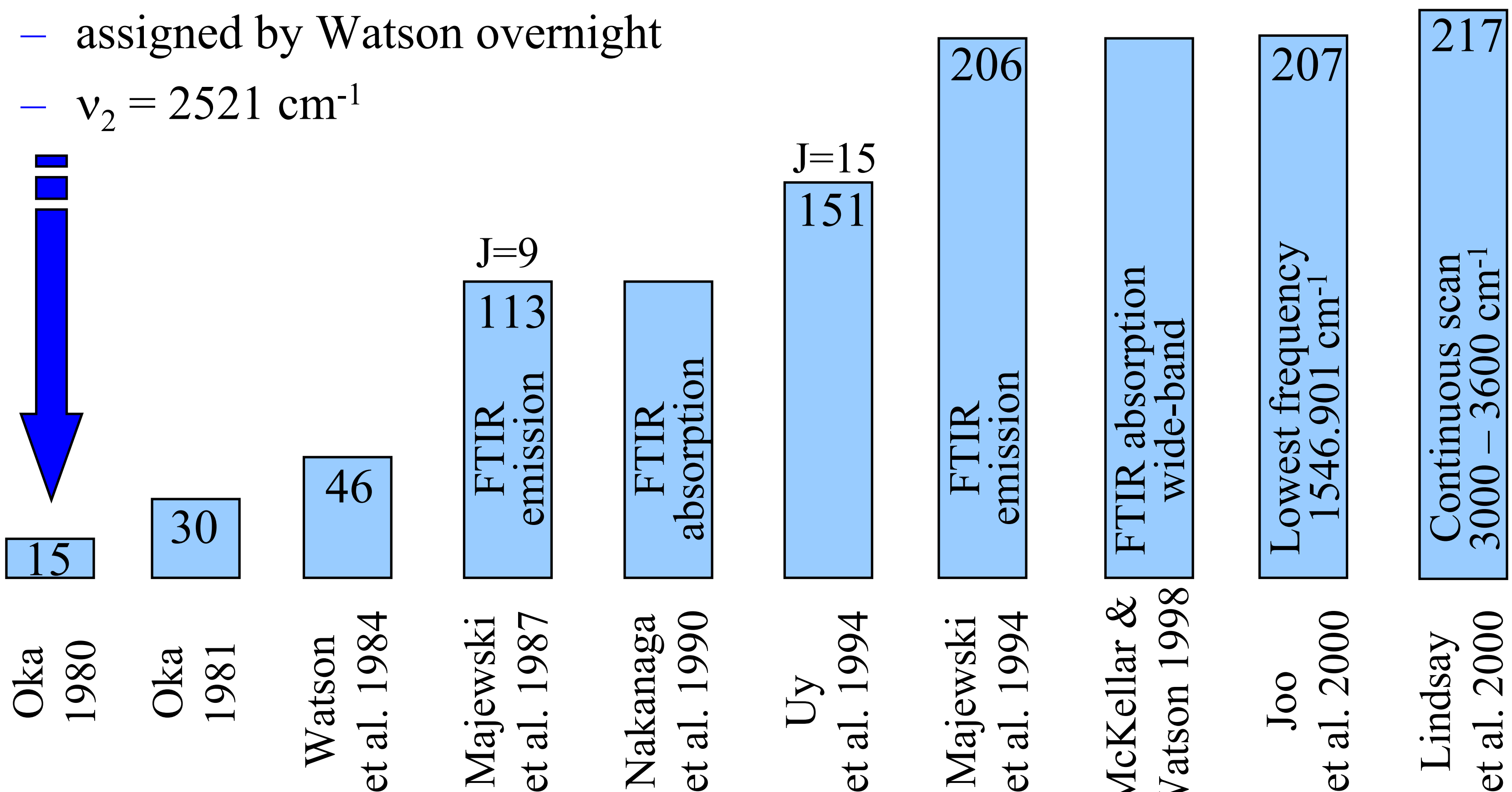
Experimental work on $\nu_2 \leftarrow 0$

- Initial Detection (Oka 1980)
  - search over two years, over 500 cm^{-1}
  - 15 lines, few percent deep
  - assigned by Watson overnight
  - ν_2 = 2521 cm^{-1}



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The $\nu_2 \leftarrow 0$ band as a probe of H_3^+

- Laboratory
  - H_3^+ electron recombination rate (Amano 1988)
  - spin conversion of H_3^+ in reactions (Uy et al. 1997)
  - ambipolar diffusion in plasmas (Lindsay, poster)
- Astronomy
  - probe of planetary ionospheres (Connerney, Miller)
  - confirmation of interstellar chemistry (Herbst)
  - measurements of interstellar clouds (Geballe)

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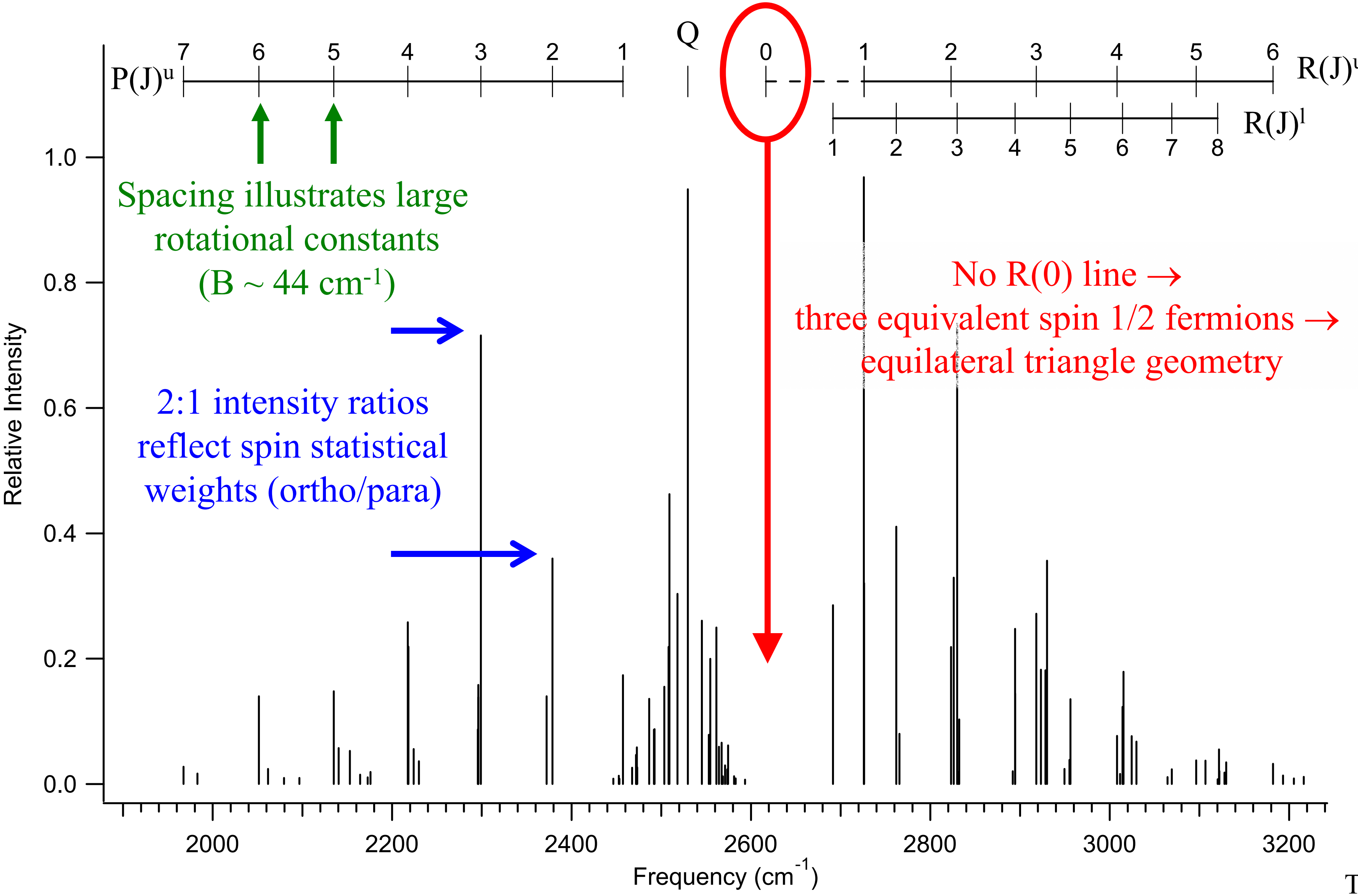
The fundamental band

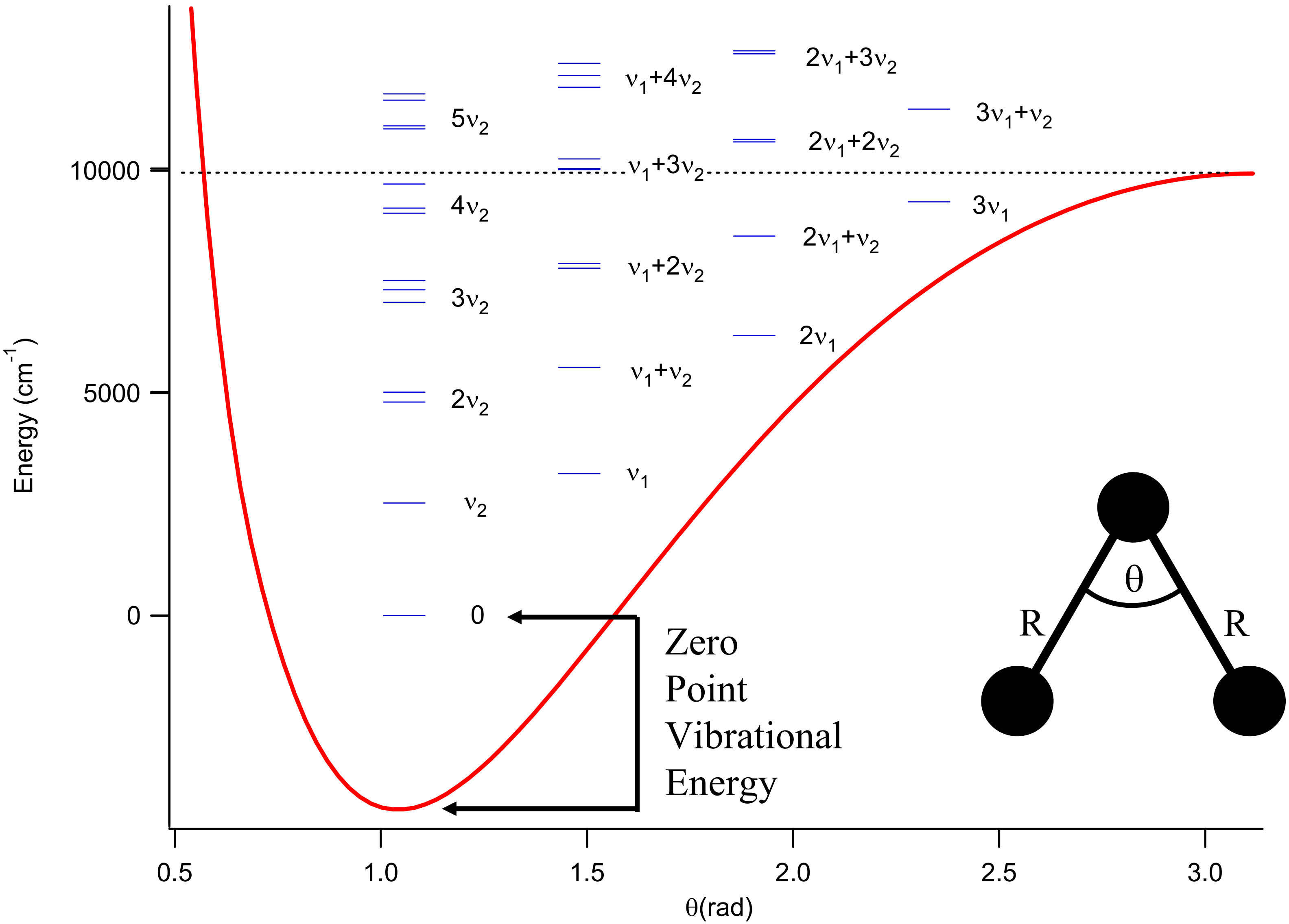


T=400 K

Understanding the ν_2 Spectrum

- For low energies, use perturbation approach:
  - $E'' = BJ(J+1) + (C-B)K^2 - D_{JK}J(J+1)K^2 + \ldots$
  - $E' = \nu_2 + B'J'(J'+1) + (C'-B')K'^2 - 2\zeta C'K'\ell + \ldots$
  - use observed transitions to fit molecular constants
  - For higher vibrational energies, this approach completely breaks down
- Variational calculations based on an *ab initio* potential energy surface!

Variational Calculations



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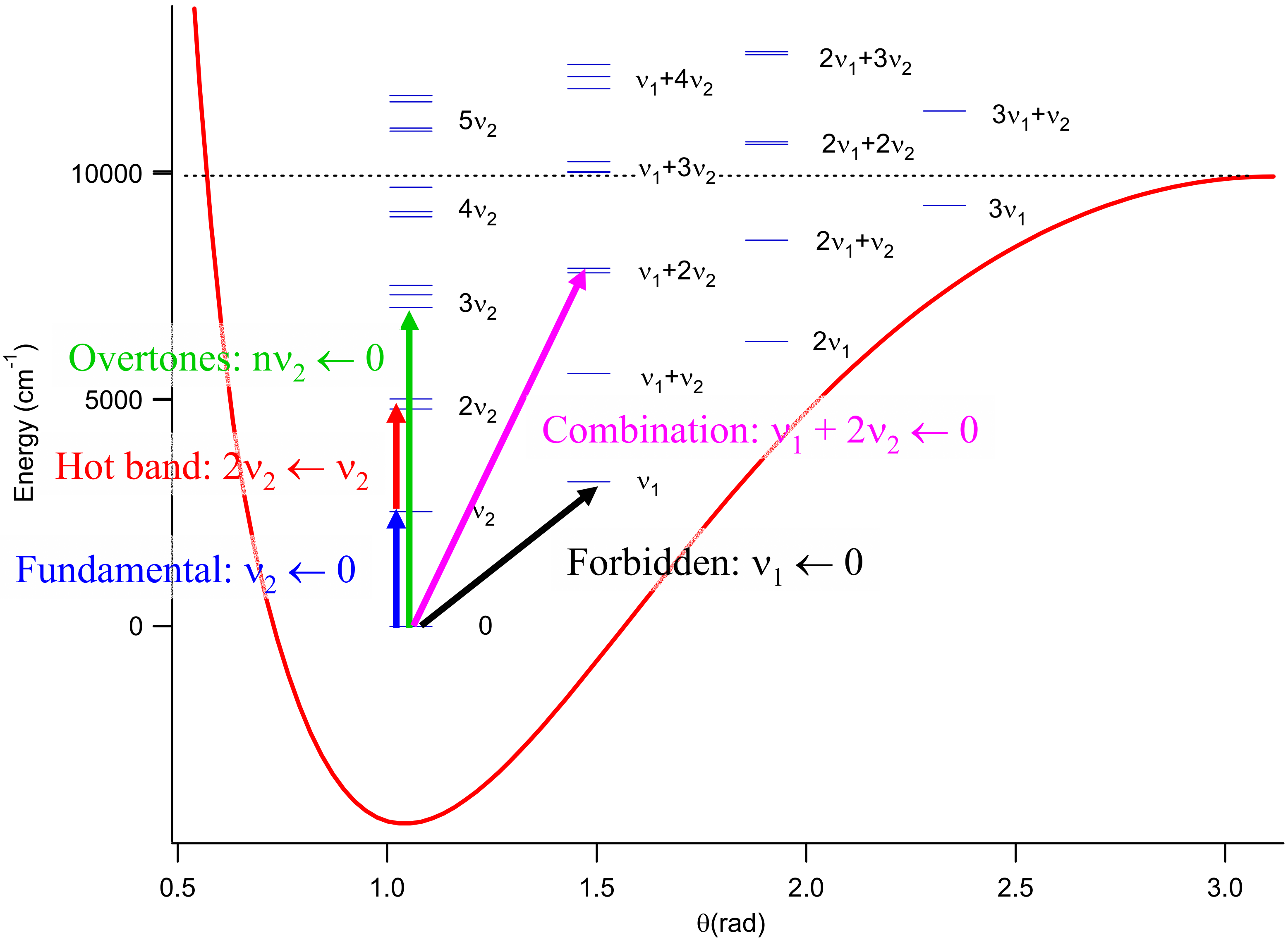
Vibrational Band Types



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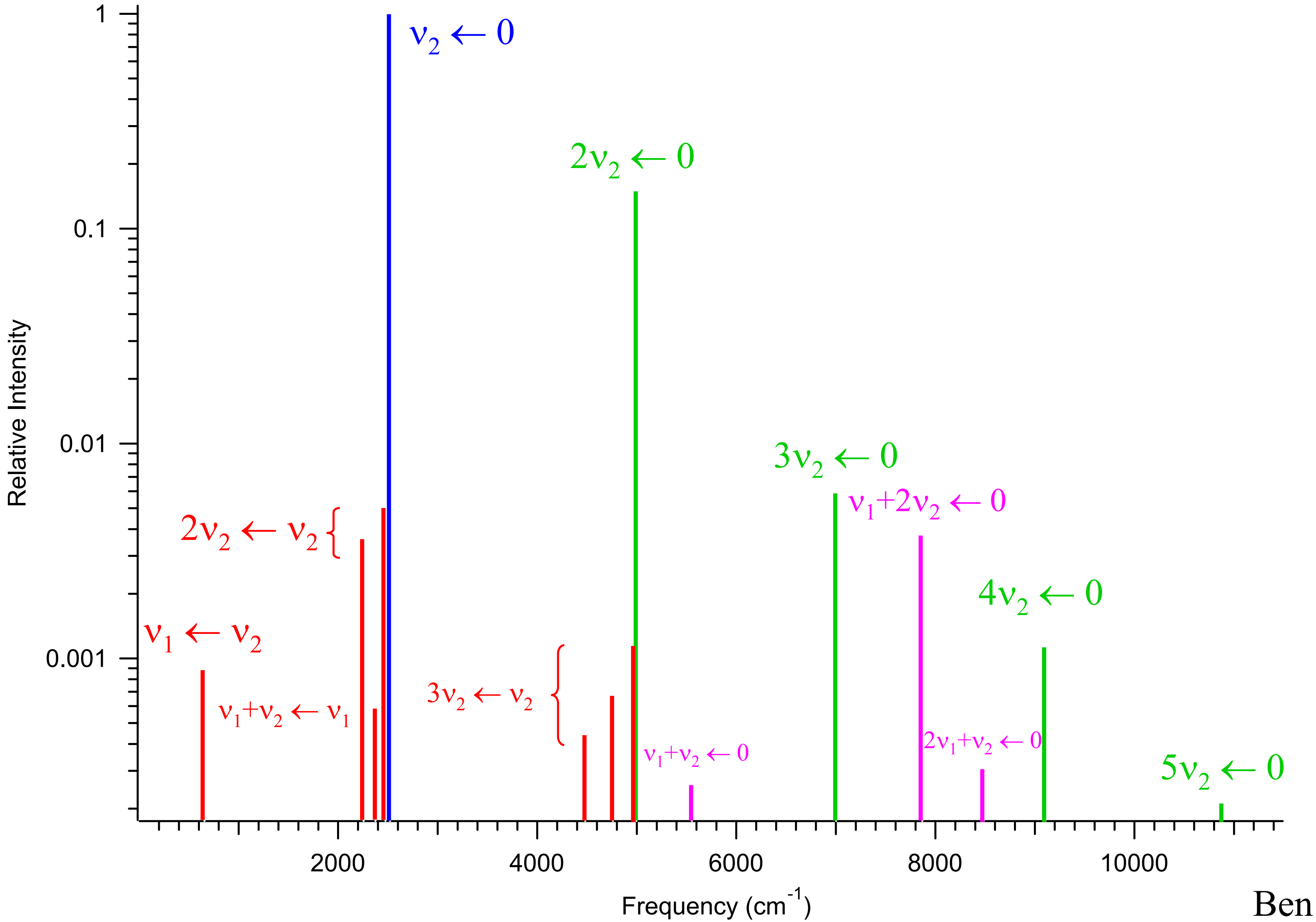
Vibrational Overview



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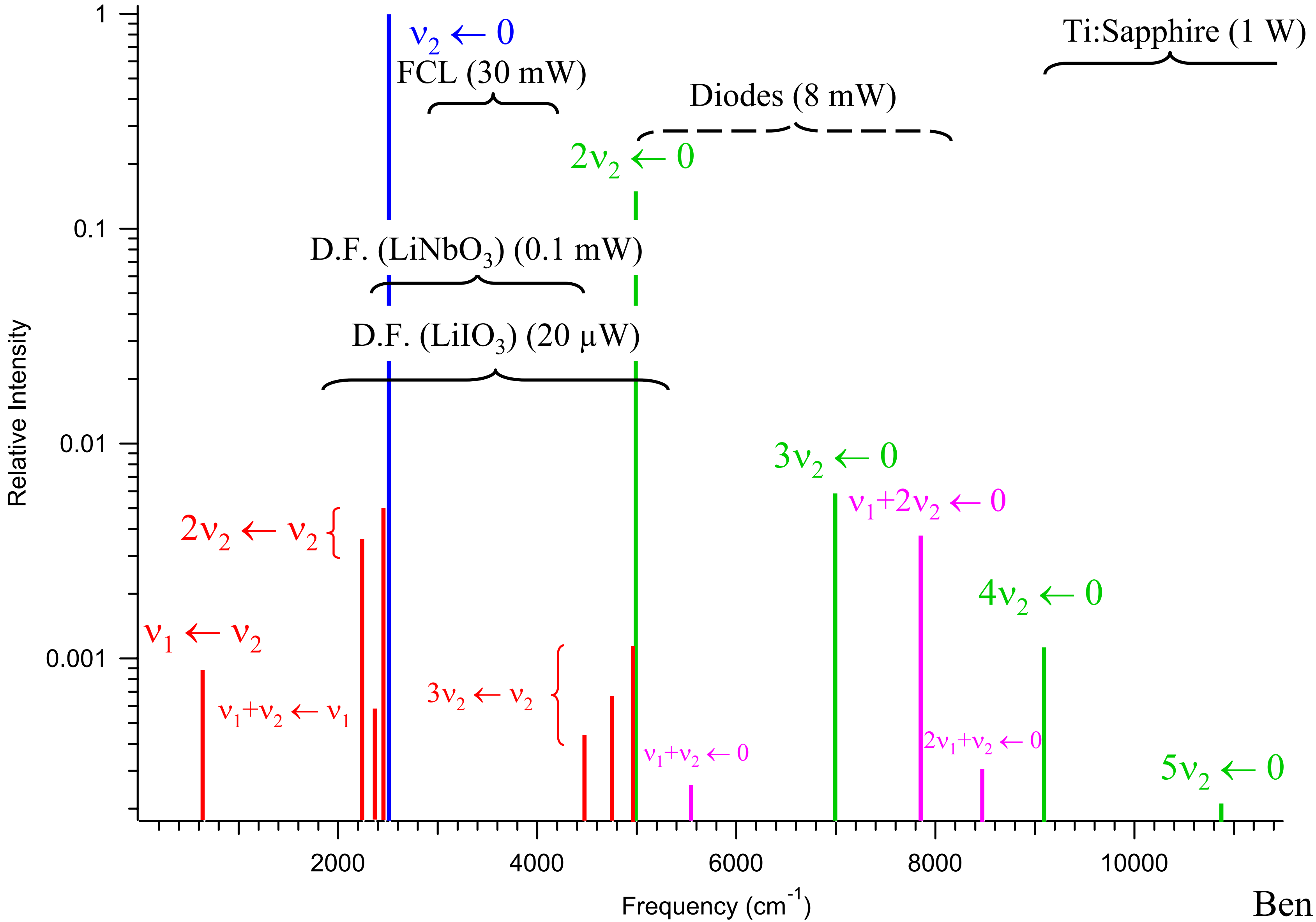
Vibrational Overview



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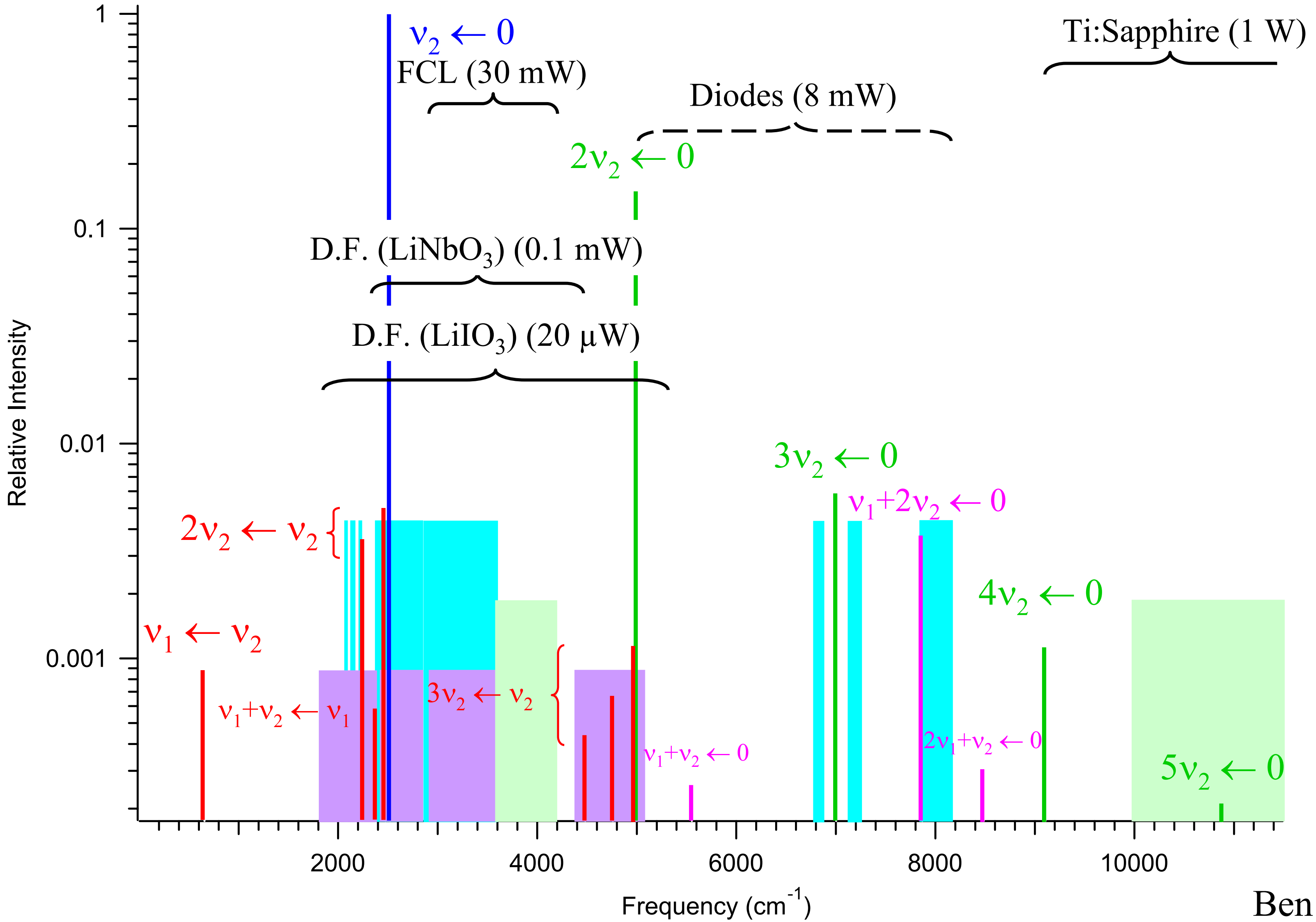
Vibrational Overview



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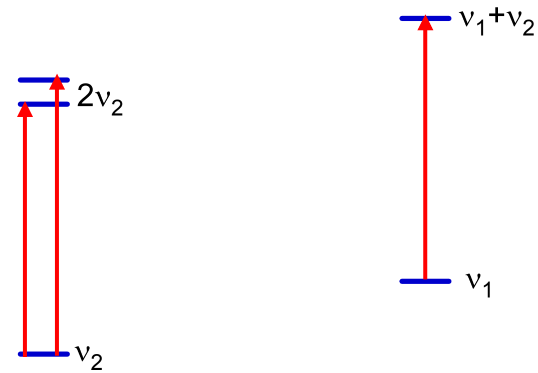
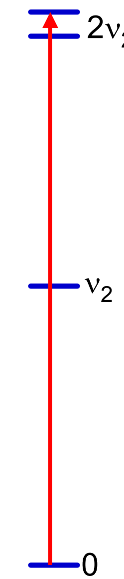
Hot Bands

- At 600 K, ~200 times weaker than fundamental
- He dominated discharge → only 50 times weaker
- Bawendi et al. (1990)
  - 72 lines of $2\nu_2^2 \leftarrow \nu_2$
  - 14 lines of $2\nu_2^0 \leftarrow \nu_2$
  - 21 lines of $\nu_1+\nu_2 \leftarrow \nu_1$



- Variational calculations essential in assignment
  - Sutcliffe 1983; Miller & Tennyson 1988, 1989

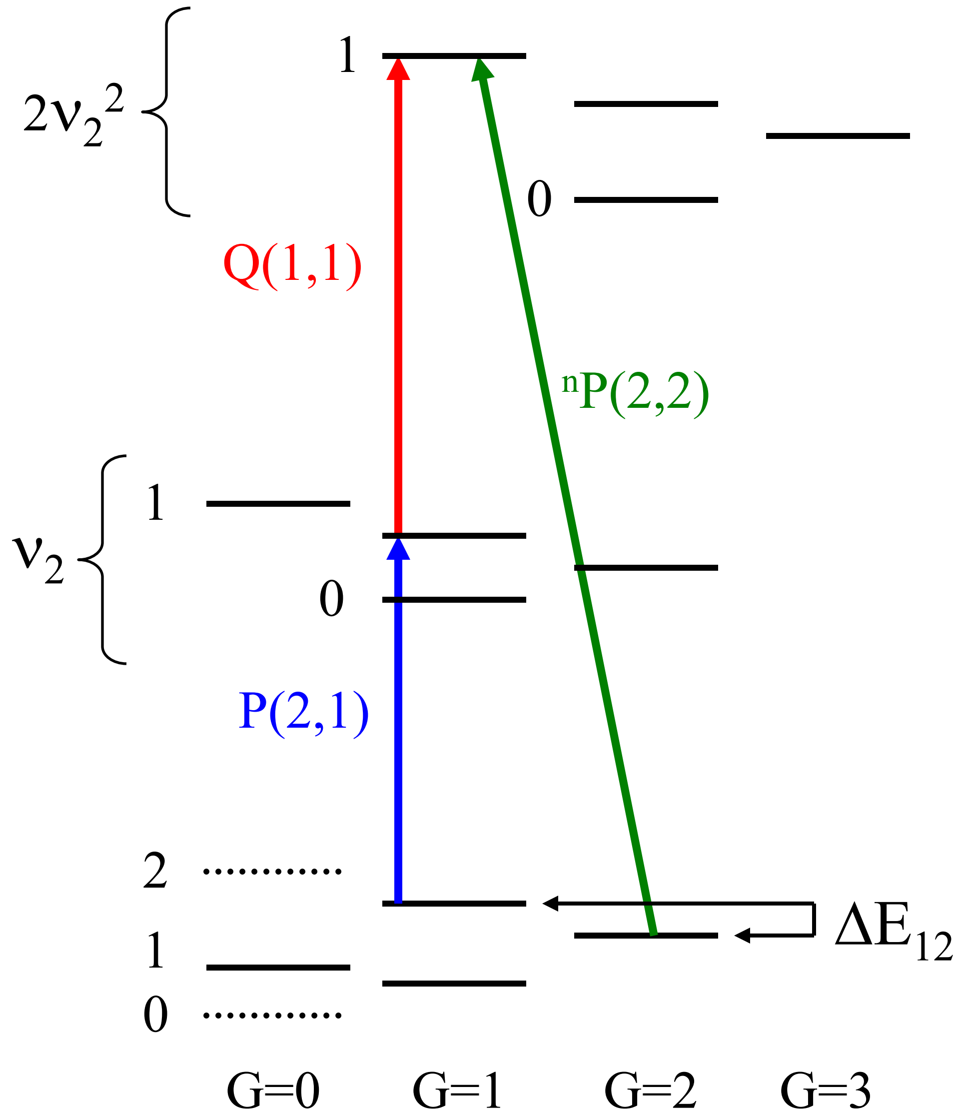
First Overtone Band: $2\nu_2 \leftarrow 0$



- First overtone ($2\nu_2 \leftarrow 0$) usually orders of magnitude weaker than fundamental
- In H_3^+, only about 7 times weaker
- Discovery:
  - (in hindsight) Majewski et al. (1987)
  - Jupiter (Trafton et al. 1989, Drossart et al. 1989)
  - Assigned by Watson (with aid of hot bands)
  - Majewski et al. (1989) – 47 transitions, FTIR
  - Xu et al. (1990) – transitions observed in absorption

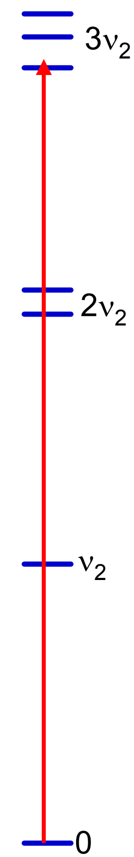
Absolute Energy Levels

- Fundamental: $\Delta G = 0$
- Hot bands: $\Delta G = 0$
- Overtone band: $\Delta G = \pm 3$
  - $(n \leftrightarrow \Delta G = -3,\ t \leftrightarrow \Delta G = +3)$
- Absolute energy levels



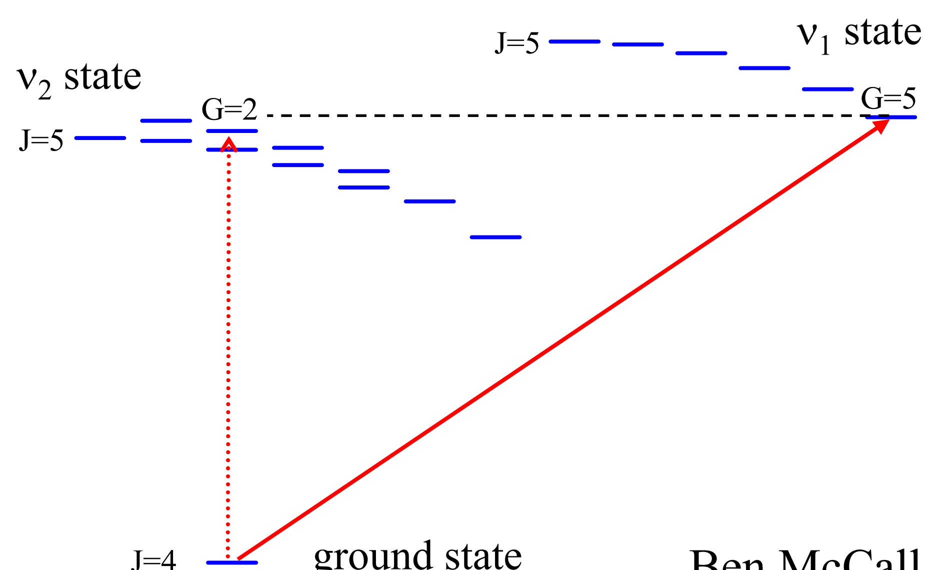
Second Overtone Band: $3\nu_2 \leftarrow 0$

- ~ 200 times weaker than fundamental
- Band origin ~ 7000 cm^{-1}
- Tunable diode lasers
- Lee et al. (1991), Ventrudo et al. (1994)
- 15 transitions observed
- Assigned based on variational calculations
  - Miller & Tennyson (1988, 1989)



Forbidden Band $\nu_1 \leftarrow 0$

- ν_1 mode totally symmetric → infrared inactive
- $\nu_1 \leftarrow 0$ very forbidden since ν_1 & ν_2 not coupled
- First mixing term: "Birss resonance"
  - mixes levels in ν_1 & ν_2 with same J, ΔG=3
  - effective for accidental degeneracies (fairly high J)
- Xu et al. (1992)
  - 9 lines
  - ν_1 = 3178 cm^{-1}
- Lindsay et al. (2000)
  - 10 new lines



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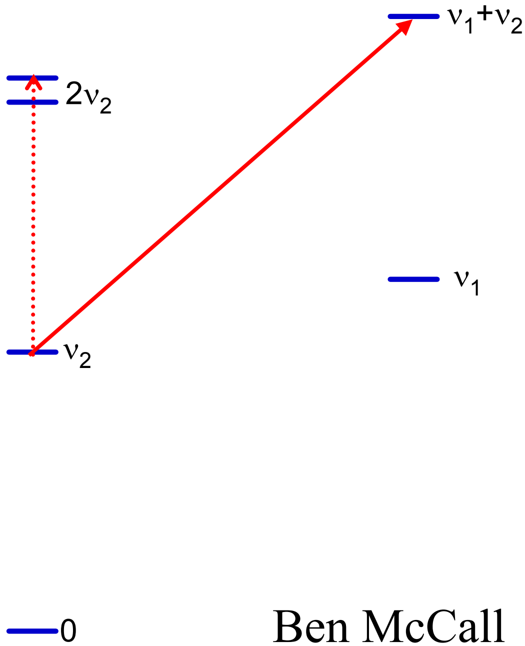
Forbidden Band $\nu_1+\nu_2 \leftarrow \nu_2$

- Not as forbidden as $\nu_1 \leftarrow 0$
  - anharmonicity of potential mixes $\nu_1+\nu_2$ with other states (e.g. $2\nu_2^2$)
  - $\nu_1+\nu_2 \leftarrow \nu_2$ can "borrow" intensity from allowed bands (e.g. $2\nu_2^2 \leftarrow \nu_2$)
- Xu et al. (1992) observed 21 lines



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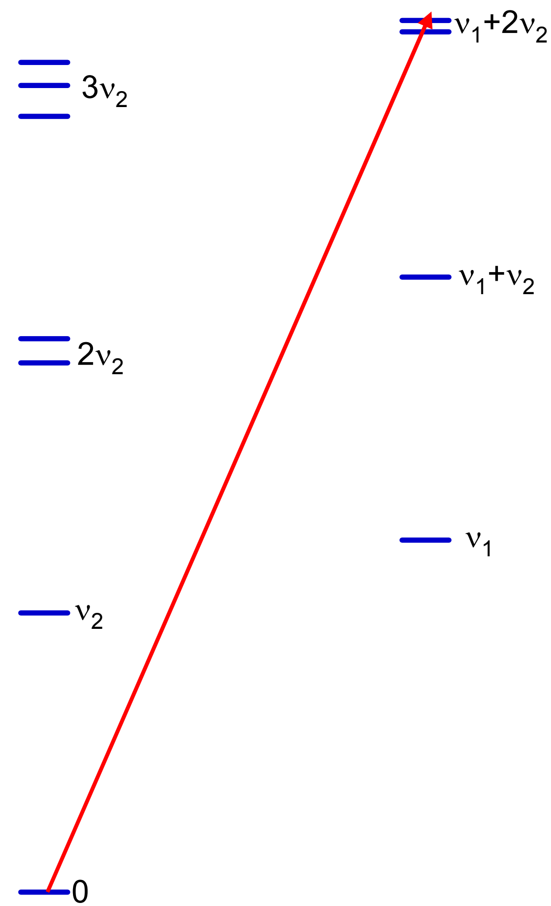
Combination Bands

- $\nu_1 + 2\nu_2^2 \leftarrow 0$

- Highest energy band
- Weakest allowed band
  - 270 times weaker than ν_2

- Tunable diode laser
  - 7780 – 8168 cm^{-1}



Observed Spectrum

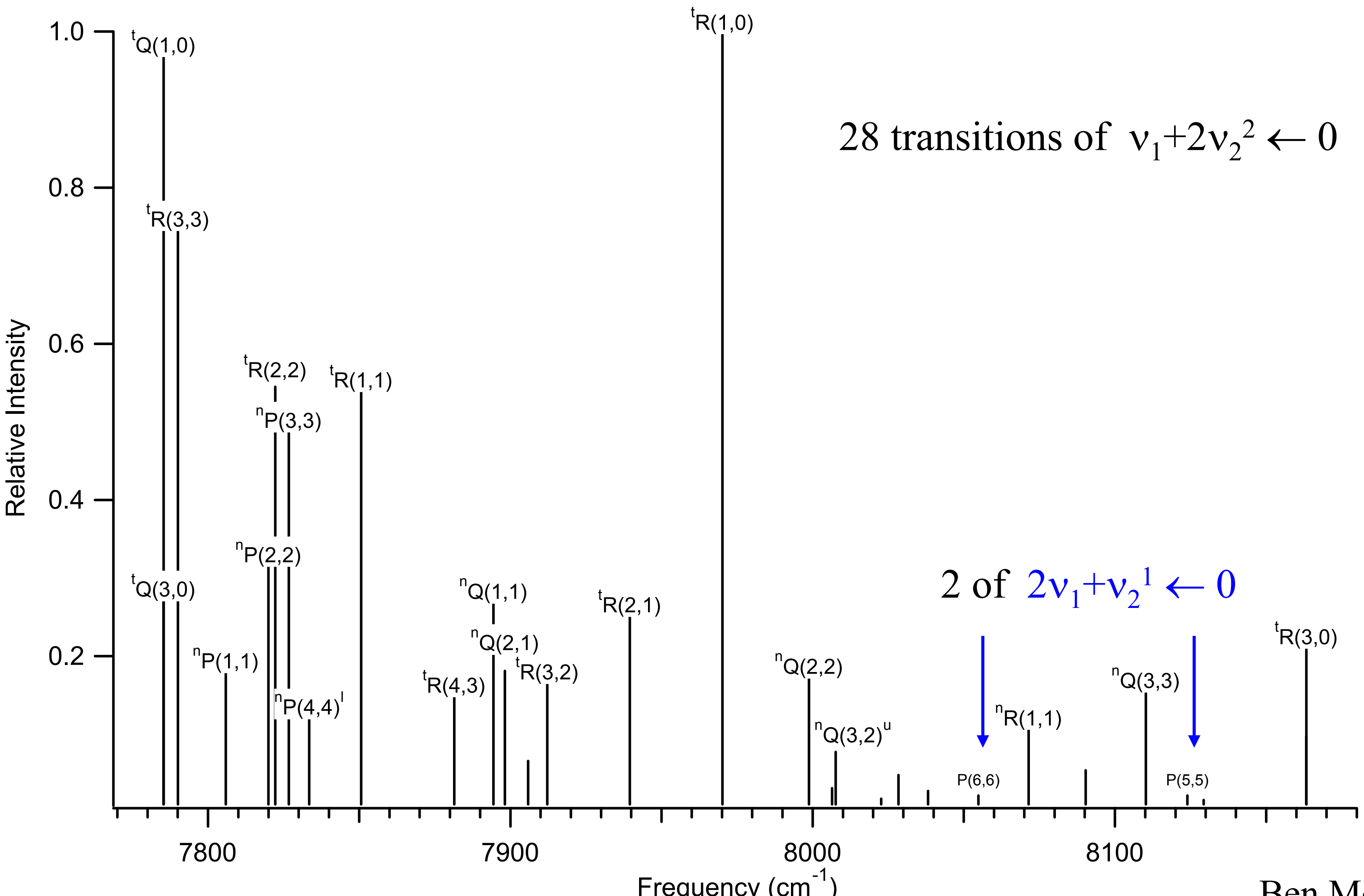


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Table of Results

Symbol	Obs	Calc	o-c	J'	<G'>	±	o/p	n'	<v1'>	<v2'>	<l2'>	J"	k"
$^{t}Q(3,0)$	7785.233	7785.264	-0.032	3	3.0	-	o	12	1.0	2.0	-2.0	3	0
$^{t}Q(1,0)$	7785.701	7785.340	0.361	1	3.0	-	o	5	1.0	2.0	-2.0	1	0
$^{t}R(3,3)$	7789.878	7790.025	-0.147	4	5.9	+	o	9	1.0	2.0	-2.0	3	3
$^{n}P(1,1)$	7805.893	7805.851	0.043	0	2.0	+	p	5	1.0	2.0	2.0	1	1
$^{n}P(2,2)$	7820.239	7819.980	0.259	1	1.0	-	p	12	1.0	2.0	2.0	2	2
$^{t}R(2,2)$	7822.375	7822.250	0.125	3	5.0	-	p	18	1.0	2.0	-2.0	2	2
$^{n}P(3,3)$	7826.739	7826.679	0.060	2	0.0	+	o	6	1.0	2.0	2.0	3	3
$^{n}P(4,4)^{l}$	7833.249	7833.444	-0.195	3	1.1	-	p	21	1.0	2.0	1.8	4	4
$^{t}R(1,1)$	7850.959	7850.677	0.283	2	4.0	+	p	15	1.0	2.0	-2.0	1	1
$^{t}R(4,3)$	7880.921	7881.443	-0.522	5	5.9	+	o	13	1.0	2.0	-2.0	4	3
$^{n}Q(1,1)$	7894.711	7894.378	0.333	1	2.0	+	p	5	1.0	2.0	2.0	1	1
$^{n}Q(2,1)$	7898.371	7898.187	0.183	2	2.0	+	p	17	1.0	2.0	2.0	2	1
$^{n}Q(3,1)$	7905.717	7905.891	-0.174	3	2.0	+	p	17	1.0	2.0	1.9	3	1
$^{t}R(3,2)$	7912.047	7912.196	-0.148	4	4.9	-	p	18	1.0	2.0	-2.0	3	2
$^{t}R(2,1)$	7939.619	7939.499	0.120	3	4.0	+	p	15	1.0	2.0	-2.0	2	1
$^{t}R(1,0)$	7970.413	7970.124	0.288	2	3.0	-	o	5	1.0	2.0	-2.0	1	0
$^{n}Q(2,2)$	7998.890	7998.754	0.136	2	1.0	-	p	12	1.0	2.0	2.0	2	2
$^{t}R(4,2)$	8005.582	8006.441	-0.858	5	4.8	-	p	30	1.0	2.0	-1.9	4	2
$^{n}Q(3,2)^{u}$	8007.410	8007.628	-0.218	3	1.0	-	p	22	1.0	2.0	1.9	3	2
$^{n}Q(4,2)^{u}$	8022.012	8022.693	-0.681	4	1.0	-	p	22	1.0	2.0	1.7	4	2
$^{t}R(3,1)$	8027.840	8028.337	-0.497	4	3.5	+	p	26	1.0	2.0	-1.8	3	1
$^{n}R(3,1)^{l}$	8037.673	8038.191	-0.518	4	2.4	+	p	27	0.9	2.1	1.7	3	1
P(6,6)	8053.382	8054.810	-1.428	5	5.5	-	o	17	1.8	1.2	-1.2	6	6
$^{n}R(1,1)$	8071.617	8071.414	0.203	2	2.0	+	p	17	1.0	2.0	2.0	1	1
$^{n}Q(4,3)$	8089.406	8090.282	-0.876	4	0.1	+	o	11	1.0	2.0	2.0	4	3
$^{n}Q(3,3)$	8110.069	8110.202	-0.133	3	0.0	+	o	11	1.0	2.0	1.8	3	3
P(5,5)	8123.128	8123.985	-0.857	4	4.8	+	p	30	1.9	1.1	-1.1	5	5
$^{t}R(4,1)$	8128.280	8129.331	-1.051	5	3.4	+	p	27	0.9	2.1	-1.8	4	1
$^{n}R(2,1)$	8163.129	8163.294	-0.165	3	2.0	+	p	17	1.0	2.0	1.9	2	1
$^{t}R(3,0)$	8162.653	8163.319	-0.666	4	2.9	-	o	12	1.0	2.0	-1.9	3	0

Predictions
from
J. K. G. Watson

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Predictions from J. K. G. Watson

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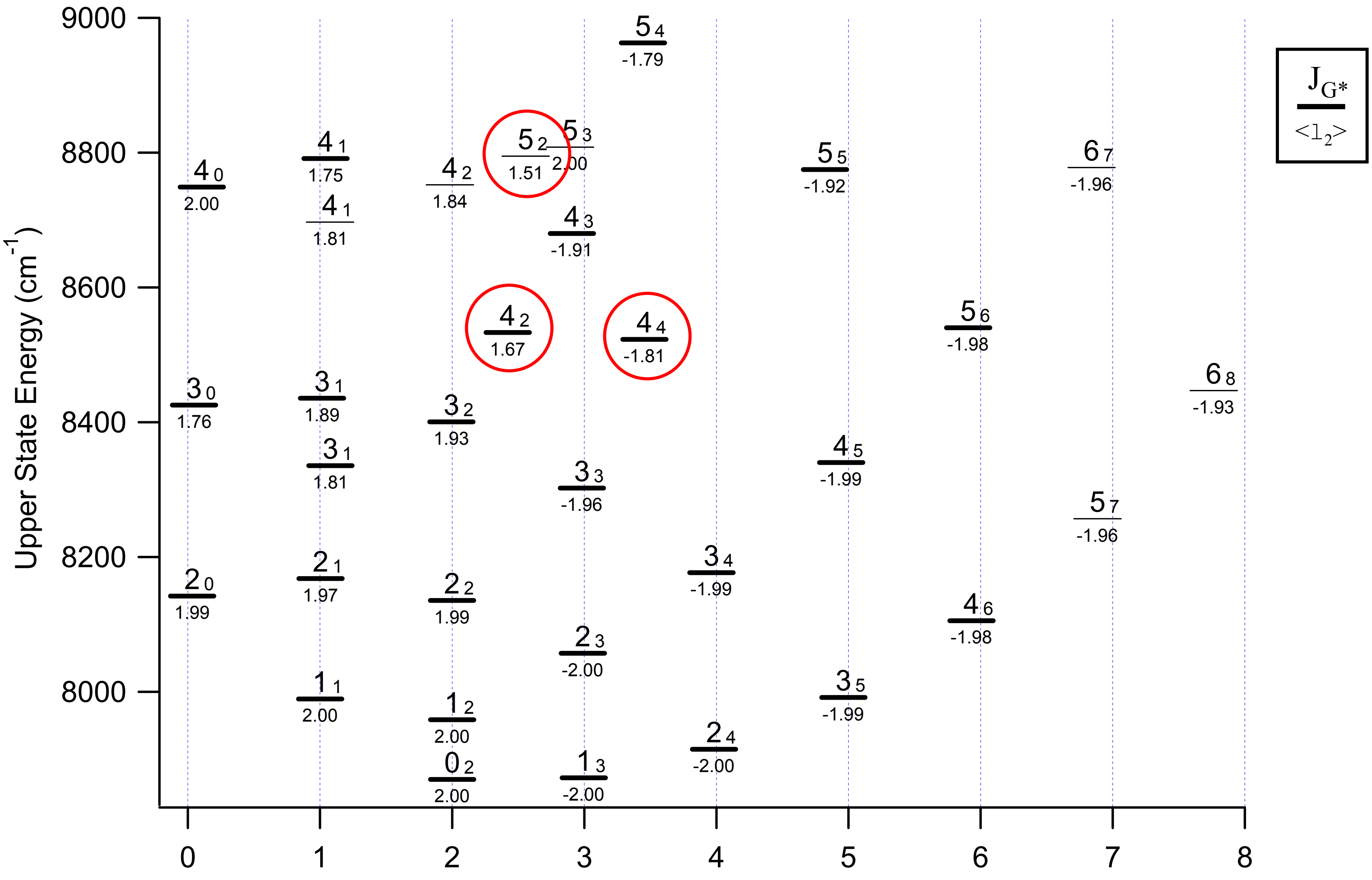
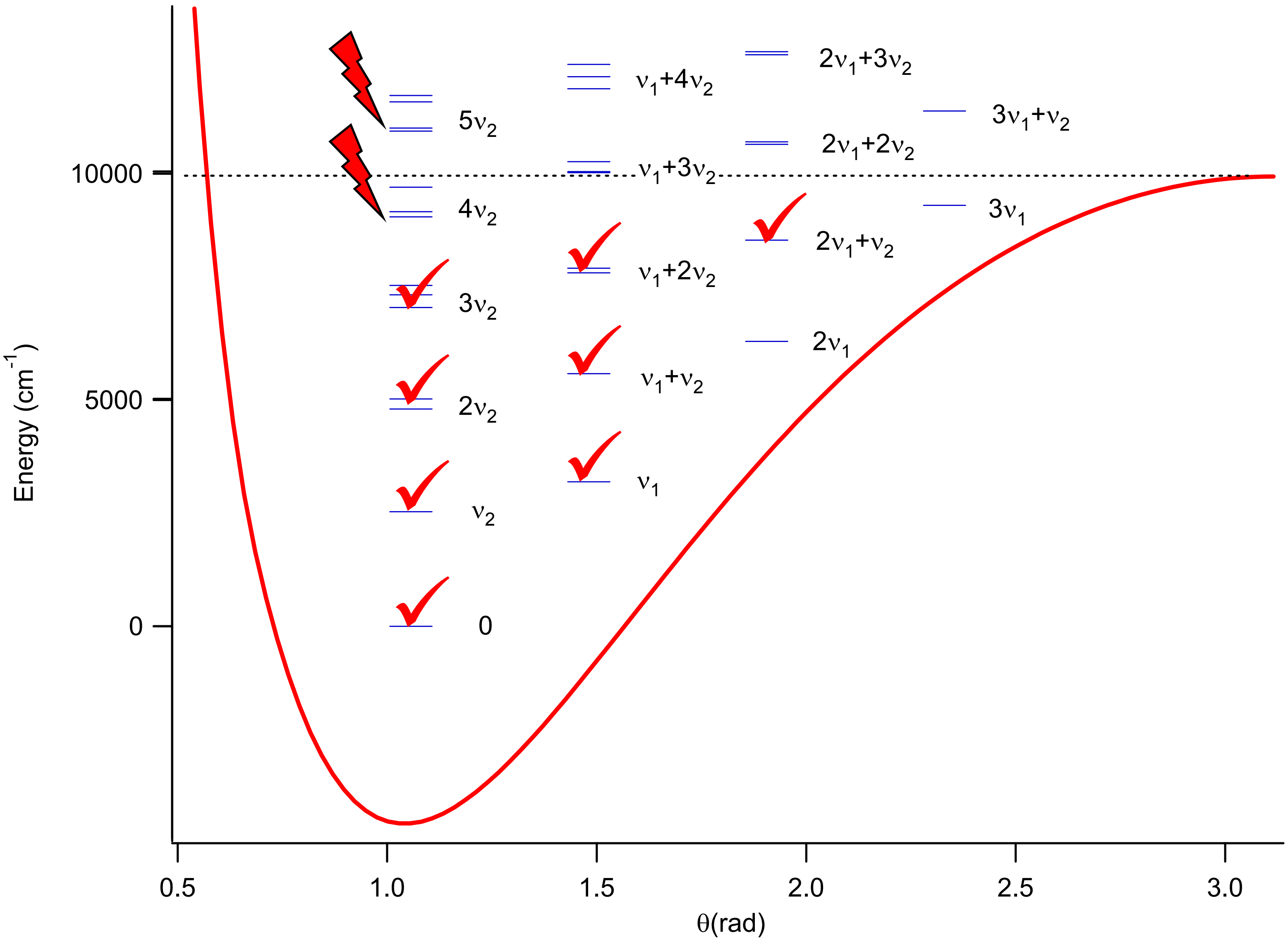
$\nu_1+2\nu_2^2$ Energy Levels



Ben McCall

Breaking the Barrier to Linearity



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Future Prospects

- Improvements in Theory
  - Hyperspherical coordinates for linearity (Watson)
  - Relativistic effects (Jaquet)
  - Non-adiabatic effects (Polyansky & Tennyson 1999)
- Experimental Advances
  - Titanium:Sapphire laser, Dye laser
  - New techniques (heterodyne, cavities?)
  - $4\nu_2 \leftarrow 0$, $5\nu_2 \leftarrow 0$ on the horizon
  - ... $10\nu_2 \leftarrow 0$ in the future??

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Column Density of H_3^+

(concentration) × (path length) ≡ Column Density

Laboratory:	10^{11} cm^{-3}	×	10^{3} cm	=	10^{14} cm^{-2}
Molecular Cloud:	10^{-4} cm^{-3}	×	10^{18} cm	=	10^{14} cm^{-2}

Laboratory and astronomical spectroscopy progressing together!

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