Using near degeneracy of molecular levels for fundamental physics

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Fundamental constants in atomic physics

Fundamental constants, which influence atomic and molecular spectra:

- Fine structure constant $\alpha = e^2/(\hbar c)$ is a coupling constant in QED.
- Electron to proton mass ratio $\mu = m_e/m_p$. Because m_p is proportional to Λ_{QCD}, $\mu \sim m_e/\Lambda_{QCD}$.
- Nuclear gyromagnetic ratio g_n can be expressed in terms of Λ_{QCD} and quark masses, but for atomic physics g_n is independent constant. It always enters in combination $g_n\mu$. According to Flambaum & Tedesco (2006) the dependence of g_n on quark masses is weak.

Dimensionless sensitivity coefficients

If fundamental constants change, the frequency of any atomic transition also change:

$$\begin{aligned} \omega &= \omega_0 \left[1 + Q_\alpha \frac{\delta\alpha}{\alpha} + Q_\mu \frac{\delta\mu}{\mu} + Q_g \frac{\delta g_n}{g_n}\right], \\ \frac{\delta\omega}{\omega} &= \frac{\delta F}{F}, \qquad F = \alpha^{Q_\alpha} \mu^{Q_\mu} g_n^{Q_g}. \end{aligned}$$

In order to detect this variation we need to compare at least two transition frequencies:

$$\frac{\omega_i}{\omega_k} = \left(\frac{\omega_i}{\omega_k}\right)_0 \left[1 + \Delta Q_\alpha \frac{\delta\alpha}{\alpha} + \Delta Q_\mu \frac{\delta\mu}{\mu} + \Delta Q_g \frac{\delta g_n}{g_n}\right].$$

Sensitivity coefficients for different wavebands (in a.u.)

- For optical transitions in atoms and molecules with nuclear charge $Z \leq 30$, all sensitivities are small, $Q_\alpha, Q_\mu, Q_g \ll 1$.
- Optical transitions in Highly Charged Ions: $|Q_\alpha| \gg 1$.
- Fine structure (IR, FIR): $\sim \alpha^2 \quad \Rightarrow \quad Q_\alpha = 2$.
- Vibrational structure (IR): $\sim \mu^{1/2} \quad \Rightarrow \quad Q_\mu = \frac{1}{2}$.
- Rotational structure (FIR, microwave): $Q_\mu = 1$.
- Magnetic hyperfine structure (microwave): $Q_\alpha = 2;\ Q_\mu = 1;\ Q_g = 1$.
- Tunneling transitions in polyatomic molecules (FIR, microwave): $1 \lesssim Q_\mu \lesssim 10$.
- Microwave mixed tunneling-rotational lines: $|Q_\mu| \gg 1$.
- Microwave Λ-doublet, Ω-doublet, and K-doublet lines in linear radicals: $|Q_\alpha|, |Q_\mu| \gg 1$.

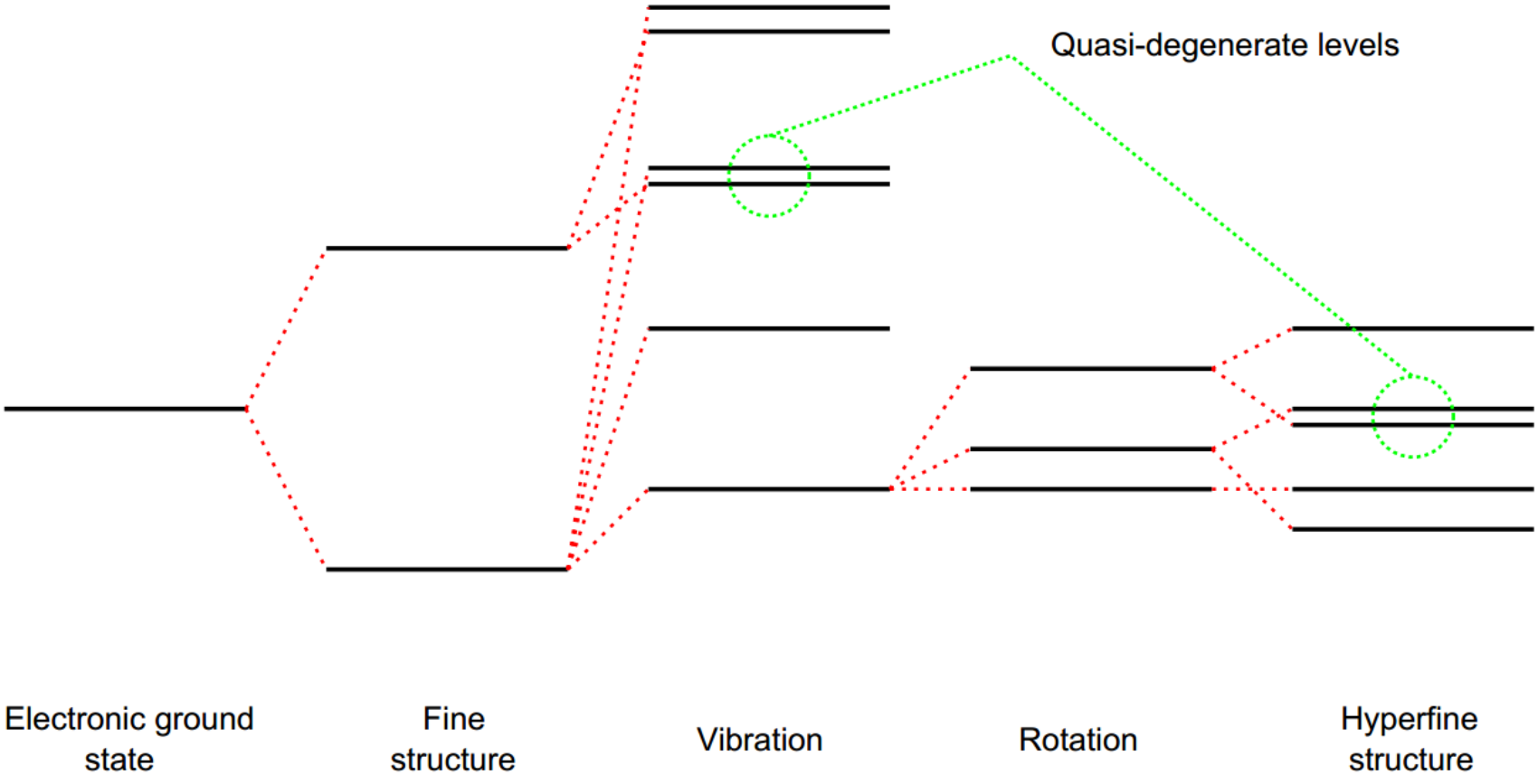
Quasi degeneracy leads to enhanced sensitivity to variation of FC

Close levels may appear due to some approximate symmetry, or because of the accidental cancellation of contributions of different nature.

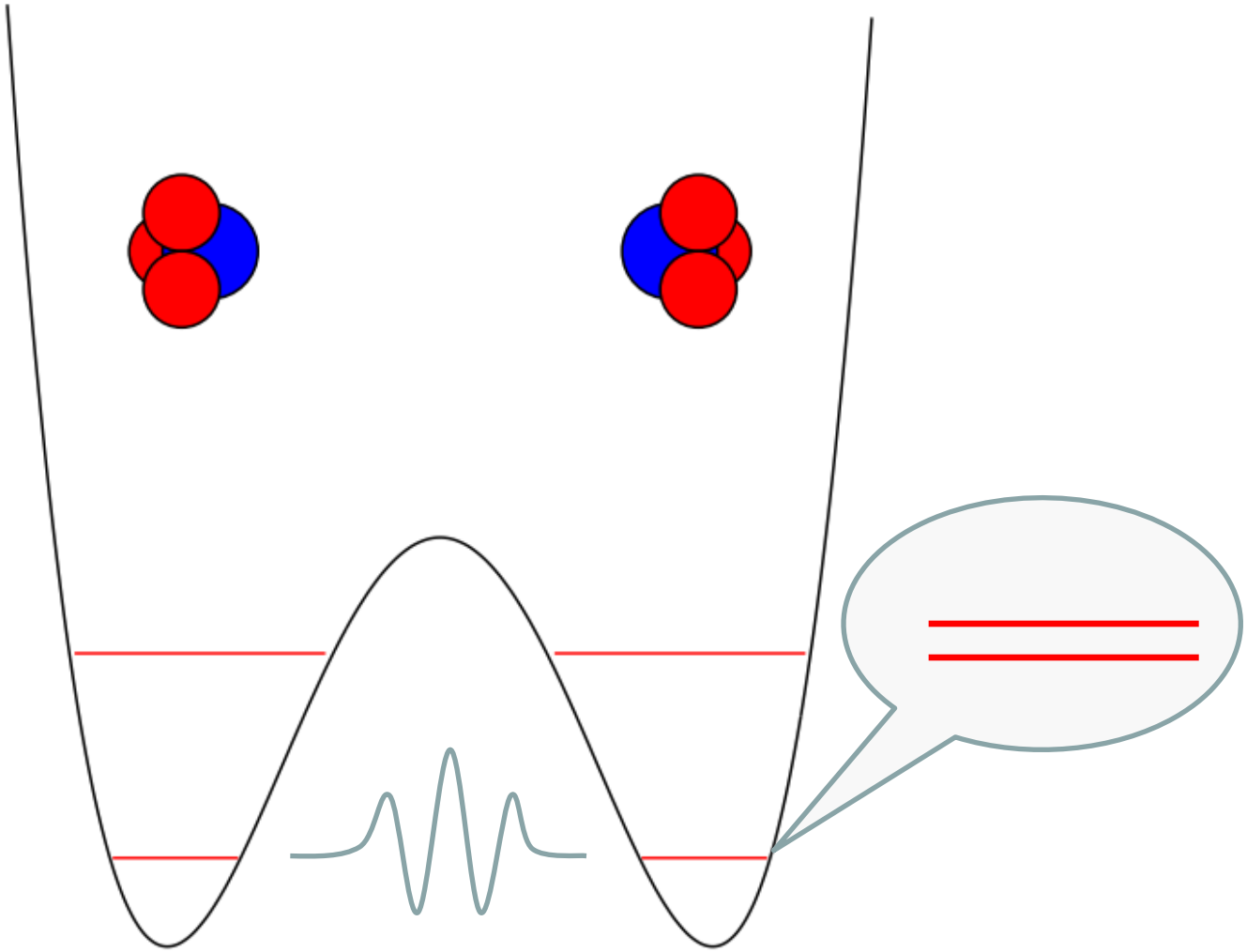
Molecules give us numerous examples of both types.

When Q-factors are important?

- Q-factors give us sensitivity to VFC when we have fixed relative accuracy of the frequency measurements.
- Q-factors are critical for high redshift astrophysics, where the lines are Doppler broadened and $\Gamma/\omega=\Delta v/c$ is independent of the waveband.
- For high precision laboratory measurements absolute shifts are important, which depend on dimensional parameters $q=Q\cdot\omega$.
- Q-factors are meaningless for indirect measurements, when small splittings are obtained as frequency differences.


Quasi-degenerate levels
Electronic ground state
Fine structure
Vibration
Rotation
Hyperfine structure

Inversion line in NH_3



Analytical solution [Landau & Lifshitz]

WKB approximation for tunneling frequency in the ground state E_0 reads:

$$\omega_{\text{tun}} = \frac{2E_0}{\pi} \exp(-S)$$

$$= \frac{2E_0}{\pi} \exp\left(-\frac{1}{\hbar}\int_{-a}^{a} \sqrt{2M_1(U(x)-E_0)}\,\mathrm{d}x\right),$$

$$\frac{\delta\omega_{\text{tun}}}{\omega_{\text{tun}}} \approx \left(\frac{1}{2} + \frac{S}{2} + \frac{S}{2}\frac{E_0}{U_{\max}-E_0}\right)\frac{\delta\mu}{\mu} = Q_\mu \frac{\delta\mu}{\mu}.$$

Sensitivity coefficients Q_μ for inversion transition in different isotopologues of ammonia.

Molecule	Action S	Q_μ
$^{14}NH_3$	5.9	4.4
$^{15}NH_3$	6.0	4.4
$^{14}NH_2D$	6.5	4.7
$^{14}ND_2H$	7.3	5.1
$^{14}ND_3$	8.4	5.7
$^{15}ND_3$	8.5	5.7
$^{15}ND_3$ *		5.6

*) van Veldhoven *et al.* [Eur. Phys. J. D,**31**, 337 (2004)].

Mixed tunneling-rotational transitions

In some molecules tunneling mode is strongly mixed with rotational degrees of freedom. For example, in partly deuterated ammonia inversion lines have different ortho-para symmetry. Because of that inversion transition goes only in combination with rotational transitions. For such mixed transitions

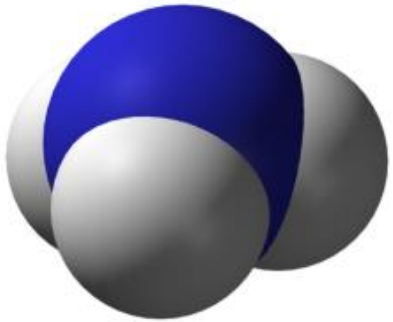
$$\omega = \omega_{\rm r} \pm \omega_{\rm tun} \,,$$

and sensitivity coefficients are equal to

$$Q_\mu = \frac{\omega_{\rm r}}{\omega} Q_{{\rm r},\mu} \pm \frac{\omega_{\rm tun}}{\omega} Q_{{\rm tun},\mu} \,,$$

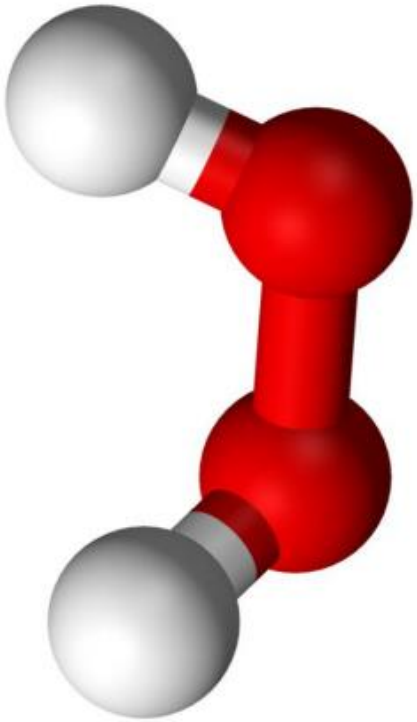
where $Q_{{\rm r},\mu} = 1$ and $Q_{{\rm tun},\mu} \gtrsim 2$. If $\omega \ll \omega_{\rm r,tun}$, then $|Q_\mu| \gg 1$.

Examples of molecules with tunneling modes



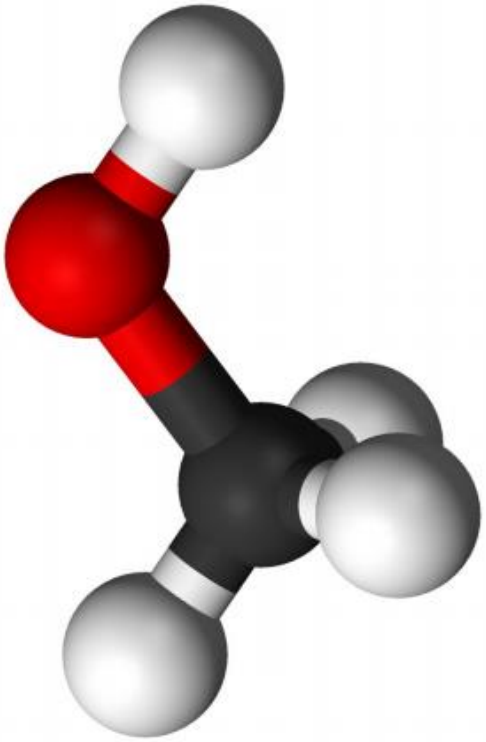
Hydronium – H_3O^+

(umbrella mode)



Peroxide – H_2O_2

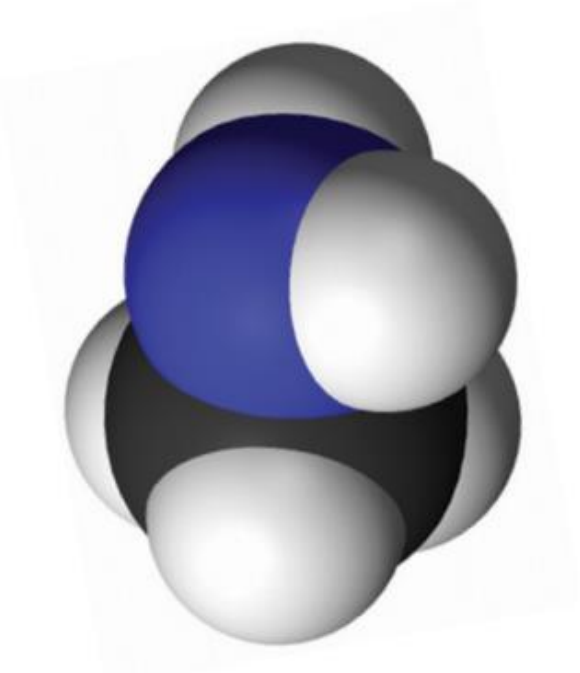
(inversion)



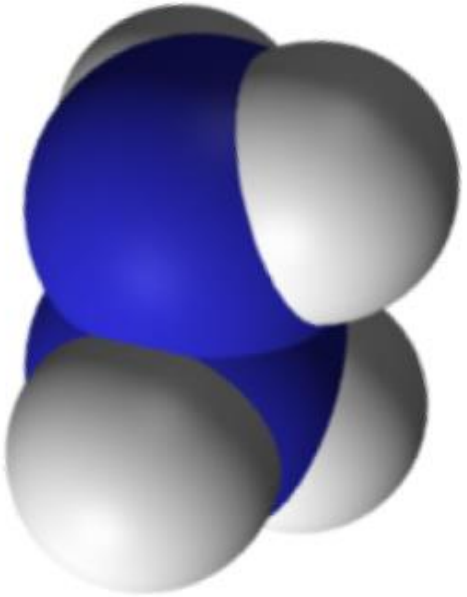
Methanol – CH_3OH

(hindered rotation)

Molecules with more than one tunneling mode



methylamine – CH_3NH_2
(one wagging & one torsion modes)



hydrazine – N_2H_4
(two wagging & one inversion modes)

Sensitivities of mixed transitions of hydronium ion

Transition						Frequency	Q_μ	ISM
J	K	s	J'	K'	s'	(MHz)		
1	1	-1	2	1	$+1$	307192.41	$+6.4$	✓
3	2	$+1$	2	2	-1	364797.43	-3.5	✓
3	1	$+1$	2	1	-1	388458.64	-3.1	✓
3	0	$+1$	2	0	-1	396272.41	-3.0	
0	0	-1	1	0	$+1$	984711.91	$+2.7$	
4	3	-1	3	3	$+1$	1031293.74	-0.6	
4	2	-1	3	2	$+1$	1069826.63	-0.5	
3	2	-1	3	2	$+1$	1621738.99	$+2.0$	
2	1	-1	2	1	$+1$	1632090.98	$+2.0$	
1	1	-1	1	1	$+1$	1655833.91	$+2.0$	

Sensitivities of mixed transitions of methanol molecule

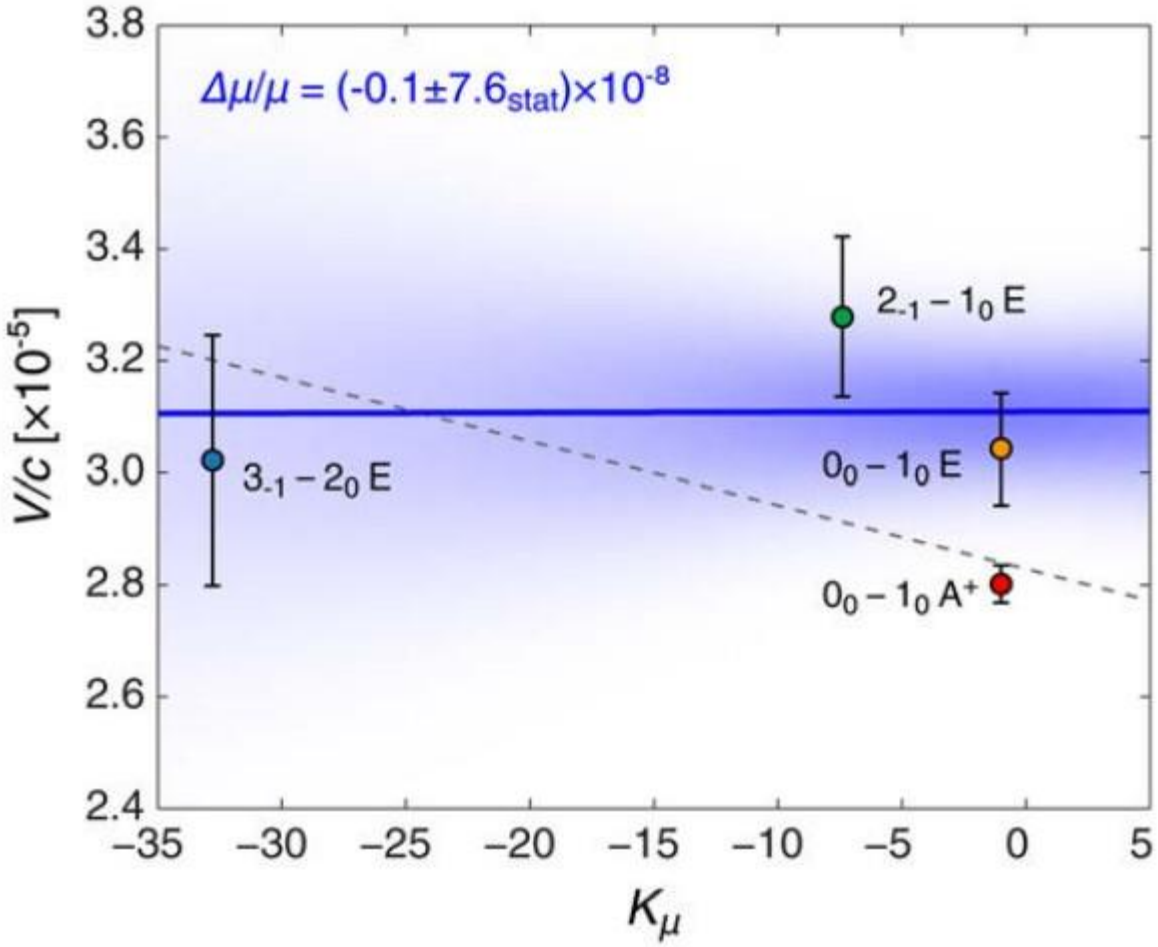
J_1	K_1	J_2	K_2	σ	ν(MHz)	T(K)	Q_μ	ISM
6	0	5	1	A^+	6669	48	+42.9	✓
3	−1	2	0	E	12179	19	+32.4	✠
3	1	3	2	E	24929	35	−16.6	✓
4	1	4	2	E	24933	43	−16.6	✓
2	1	2	2	E	24934	27	−16.6	✓
3	0	4	−1	E	36169	26	−9.6	✓
6	1	7	0	A^+	44069	63	−5.3	✓
2	−1	1	0	E	60531	13	+7.3	♠
4	0	3	1	A^+	107014	23	+3.6	✓
5	−1	5	0	E	157179	39	+3.4	✓
4	−1	4	0	E	157246	27	+3.4	✓
2	0	2	1	A^+	304208	7	+1.9	✓

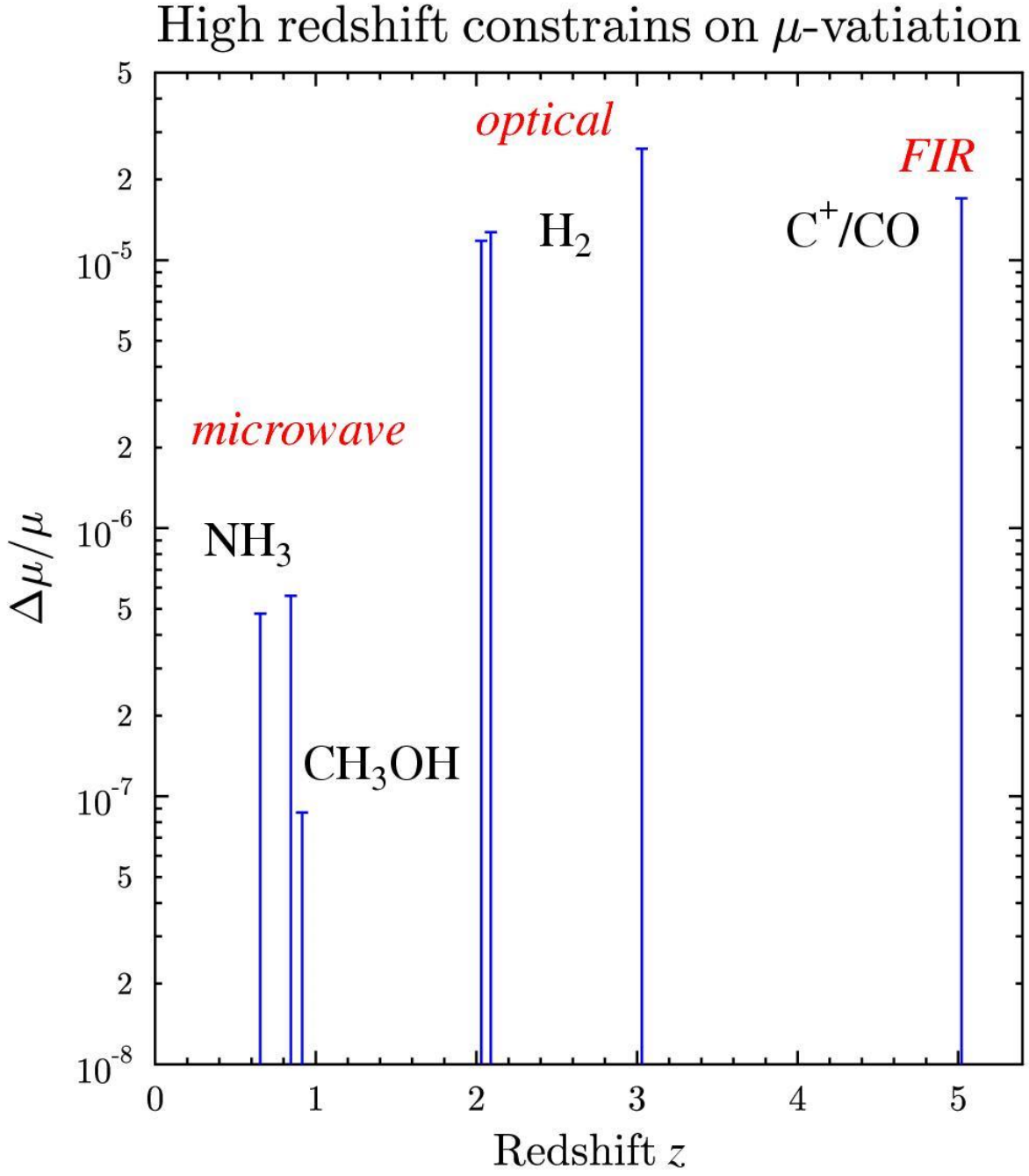
✓Milky Way; ♠ redshift $z = 0.89$ (Muller *et al.* 2011)

✠ redshift $z = 0.89$ (Ellingsen *et al.* 2012)

Constrain on μ-variation from observation of methanol lines at redshift z=0.89

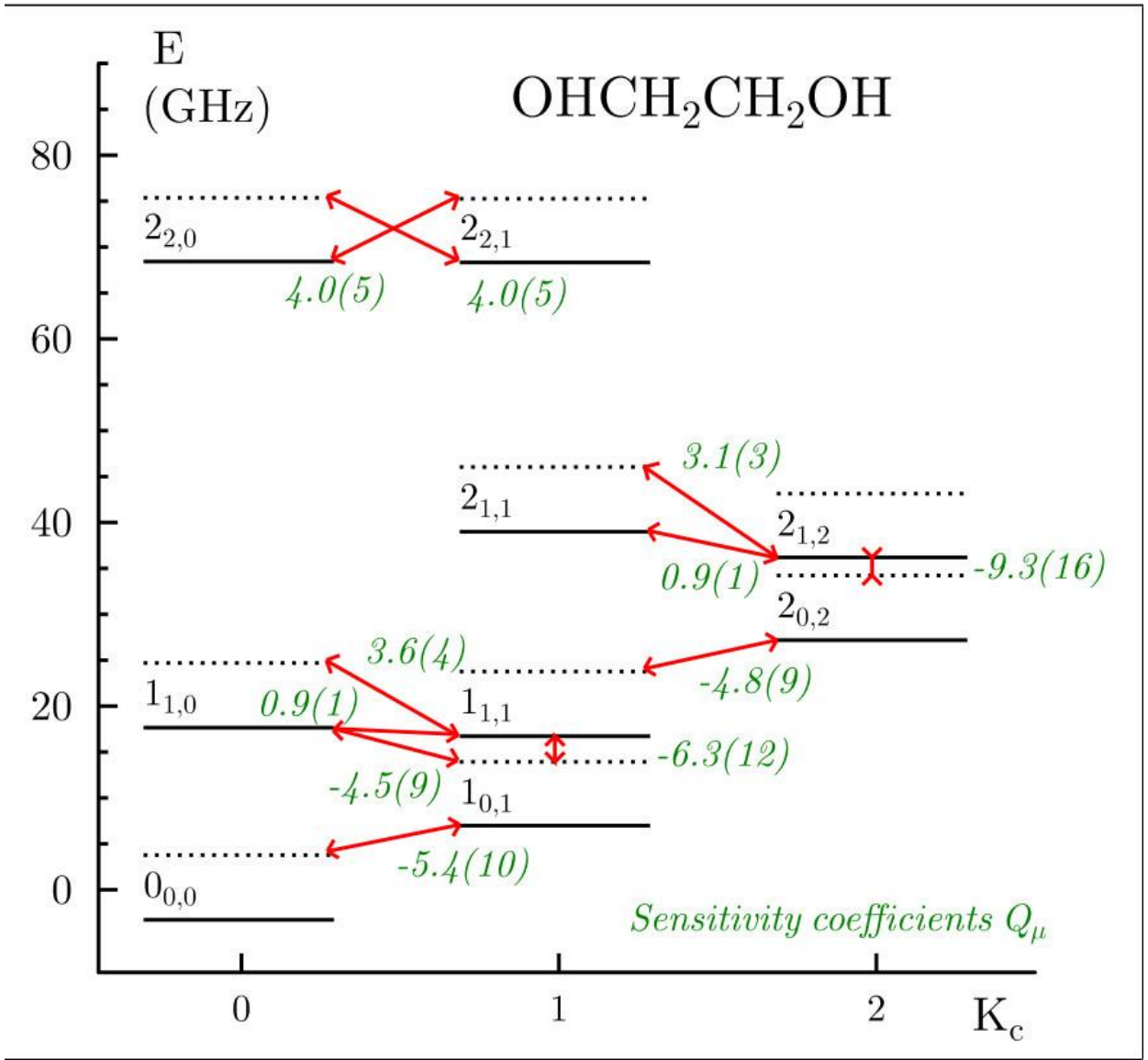
[Bagdonaite et al. Science 339, 46 (2013)]




High redshift constrains on μ-vatiation
optical
FIR
H_2
C^+/CO
microwave
NH_3
CH_3OH
$\Delta\mu/\mu$
Redshift z
5
2
10^{-5}
5
2
10^{-6}
5
2
10^{-7}
5
2
10^{-8}
0
1
2
3
4
5

Tunneling-rotational spectrum of Ethylene glycol

[A Viatkina & MK 2014]



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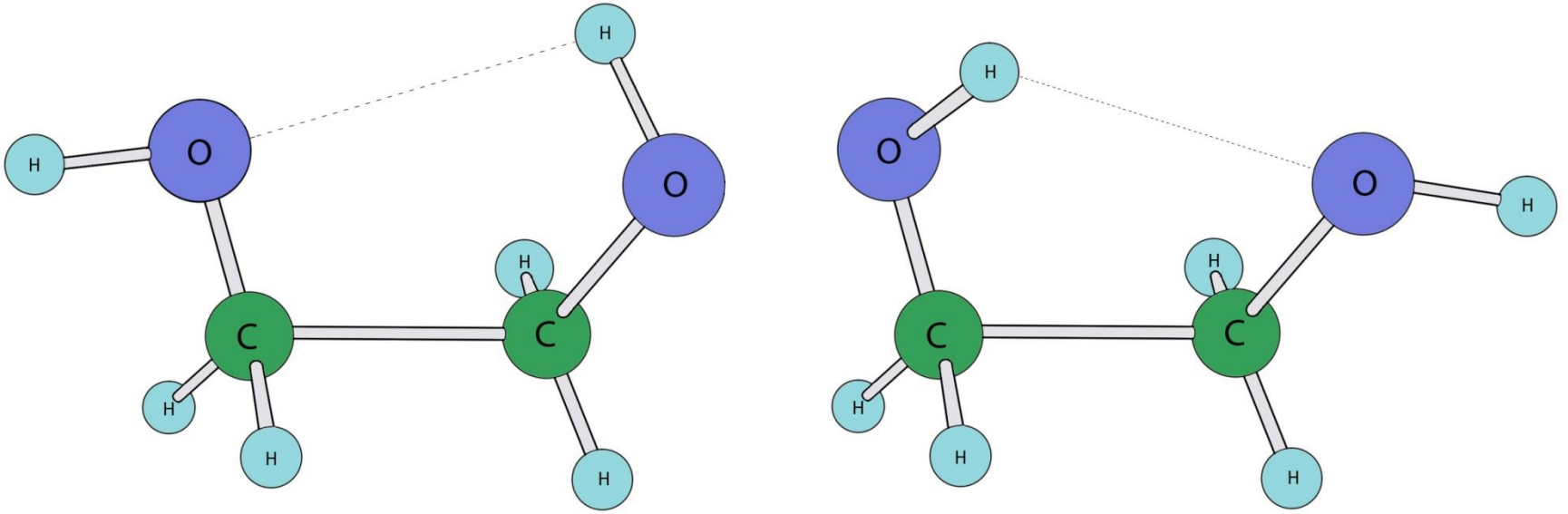
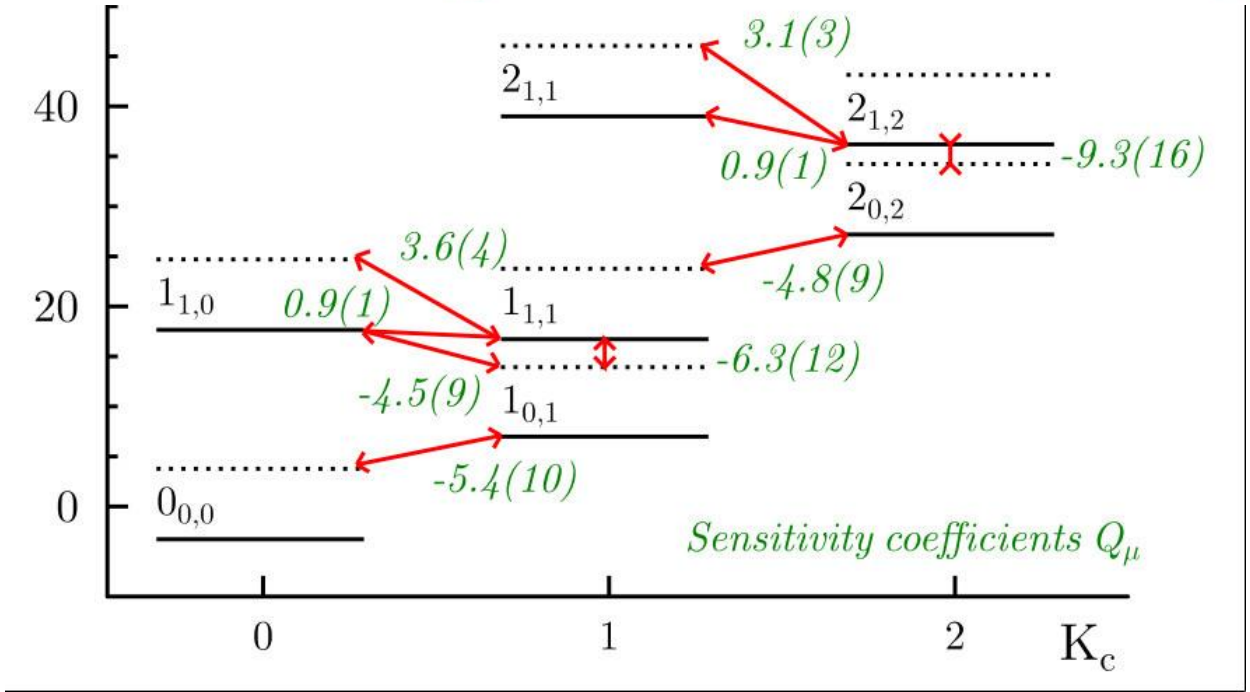
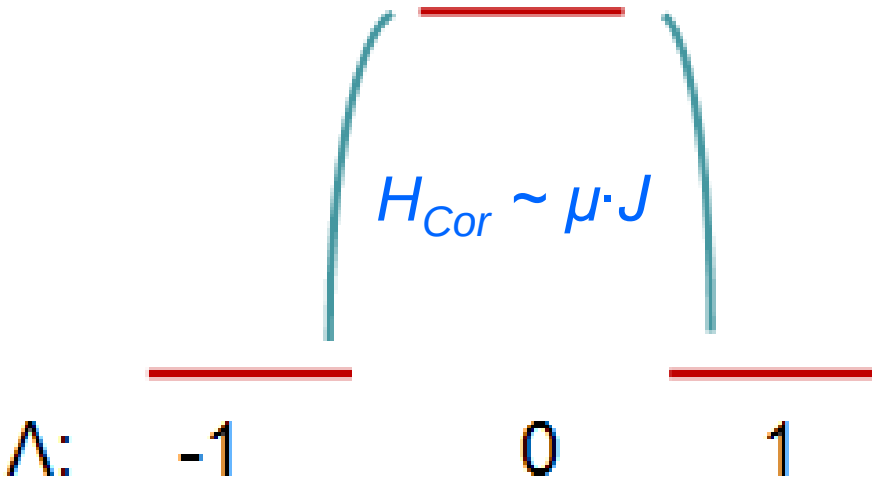




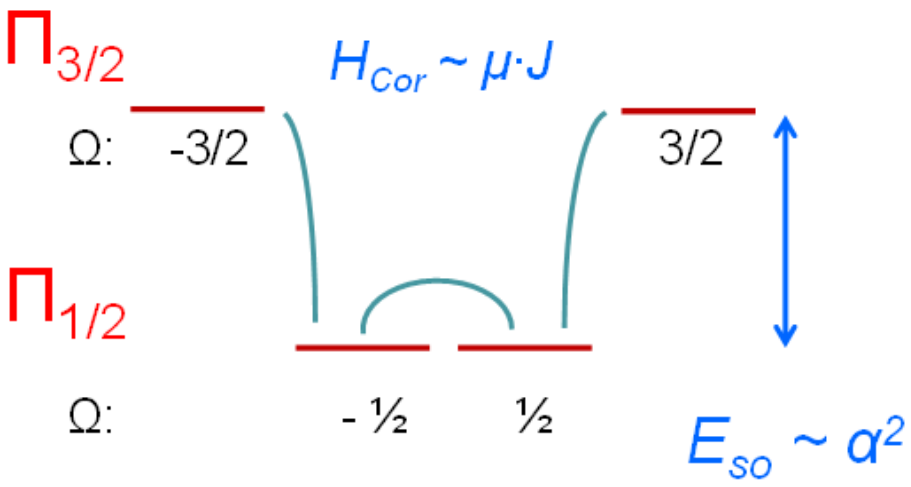
Quasi degeneracy in linear molecules: Λ-doubling & Ω-doubling.

1. Λ-doubling



$$\Delta E_{\Lambda} \sim \mu^2 J^2$$

2. Ω-doubling

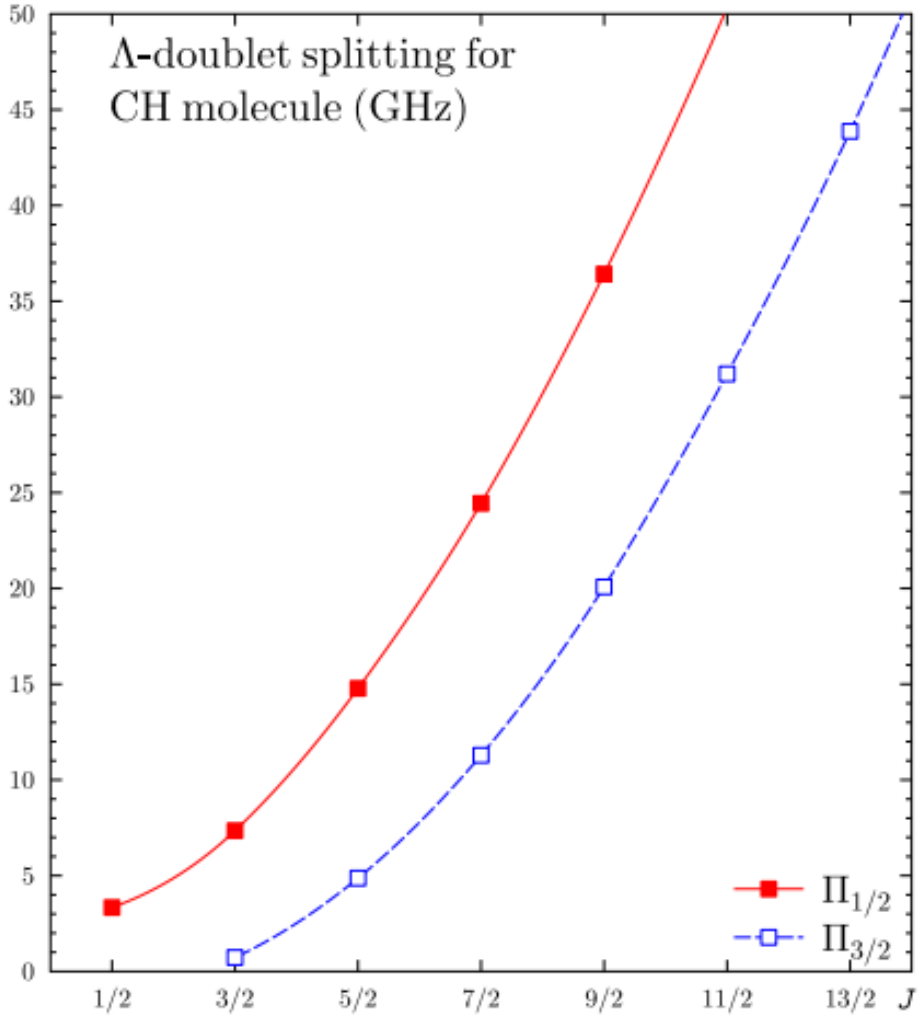


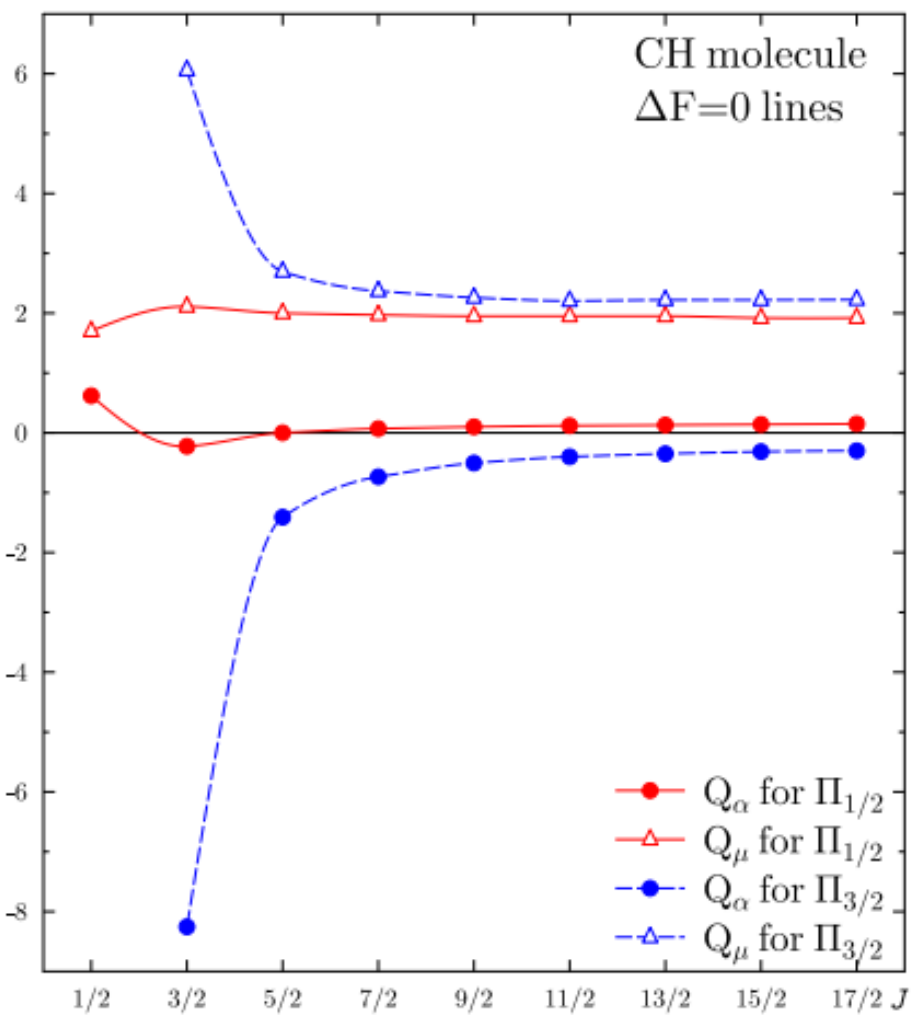
$\Delta E_{\Omega}(\Pi_{3/2}) \sim \mu^3 J^3/\alpha^2$

$\Delta E_{\Omega}(\Pi_{1/2}) \sim \mu\alpha^2 J$

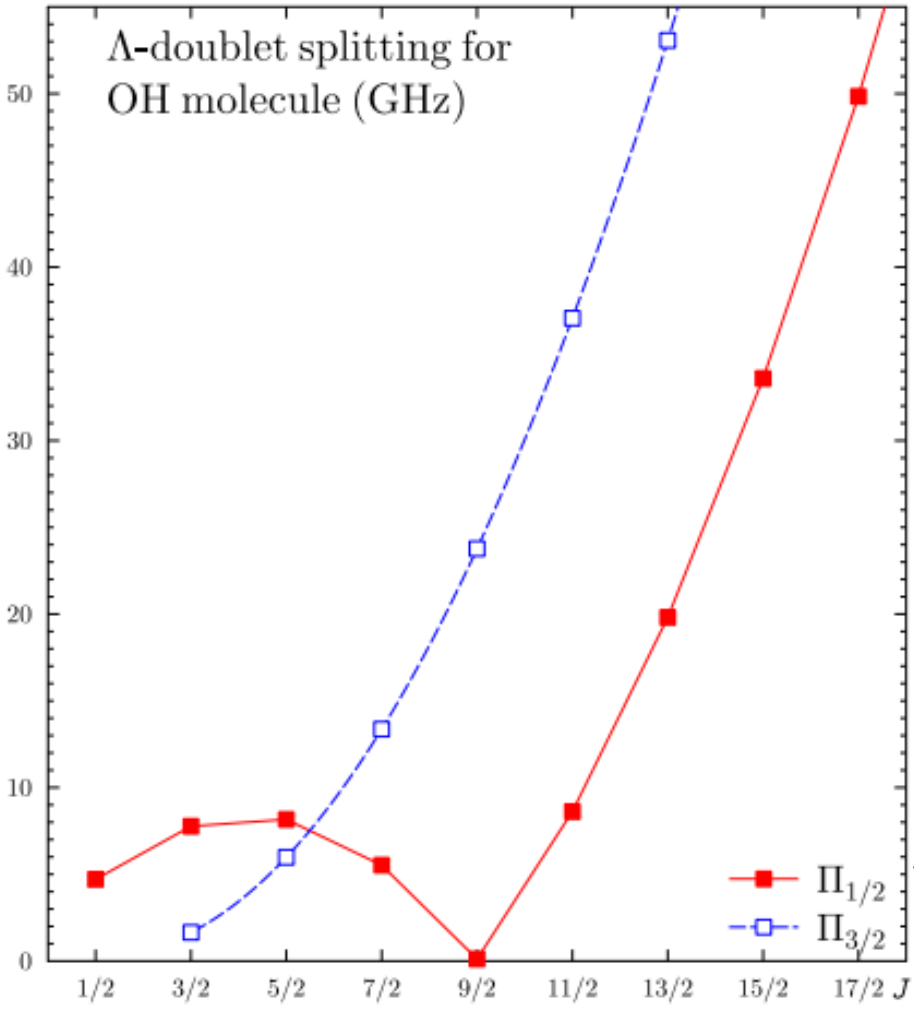
Spin-orbit interaction couples electron spin to the molecular axis. When rotational energy grows, electron spin decouples from the axis. Then quantum number Ω is substituted by Λ. Competition between Coriolis and SO interactions leads to strong dependence of the doubling splitting on α and μ.

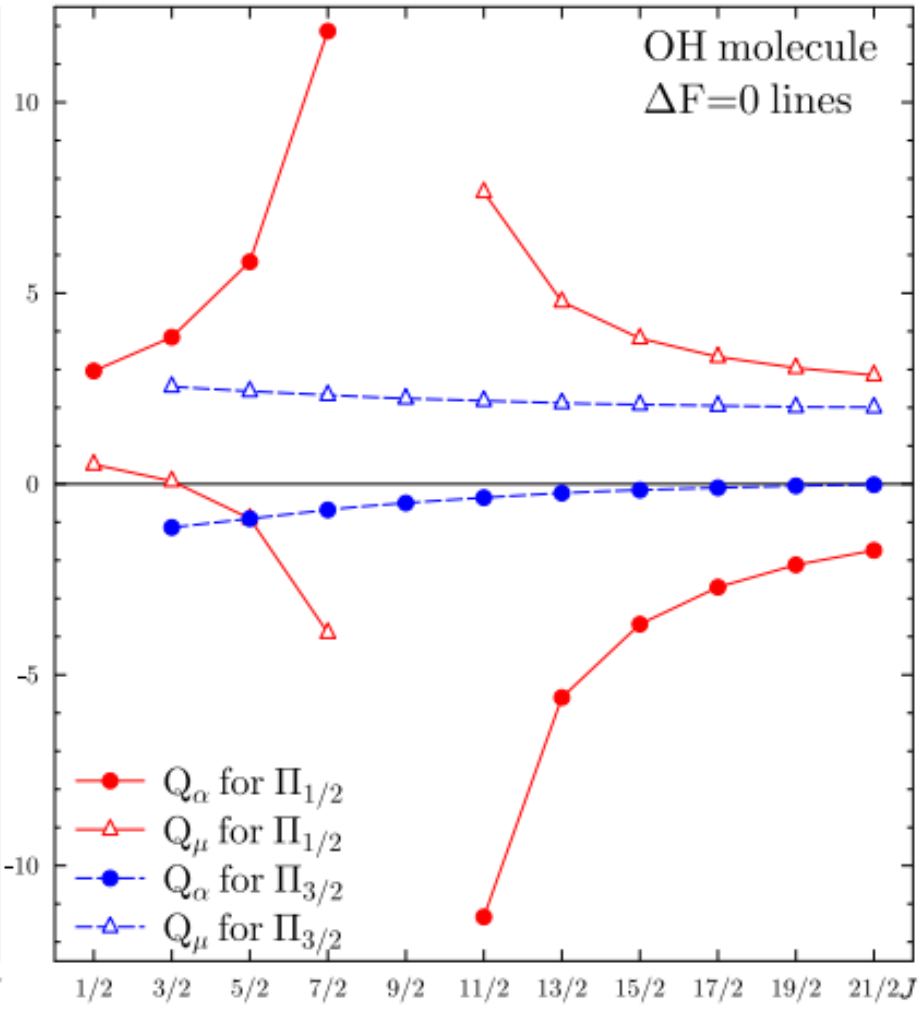
Frequencies & sensitivities of Λ-transitions in CH



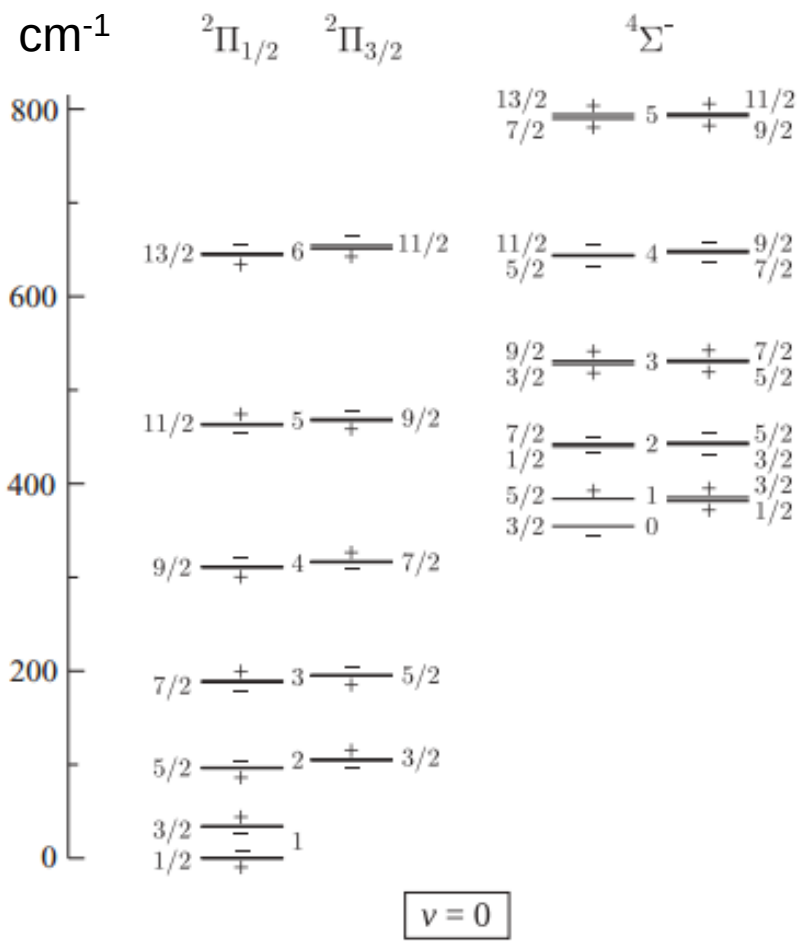


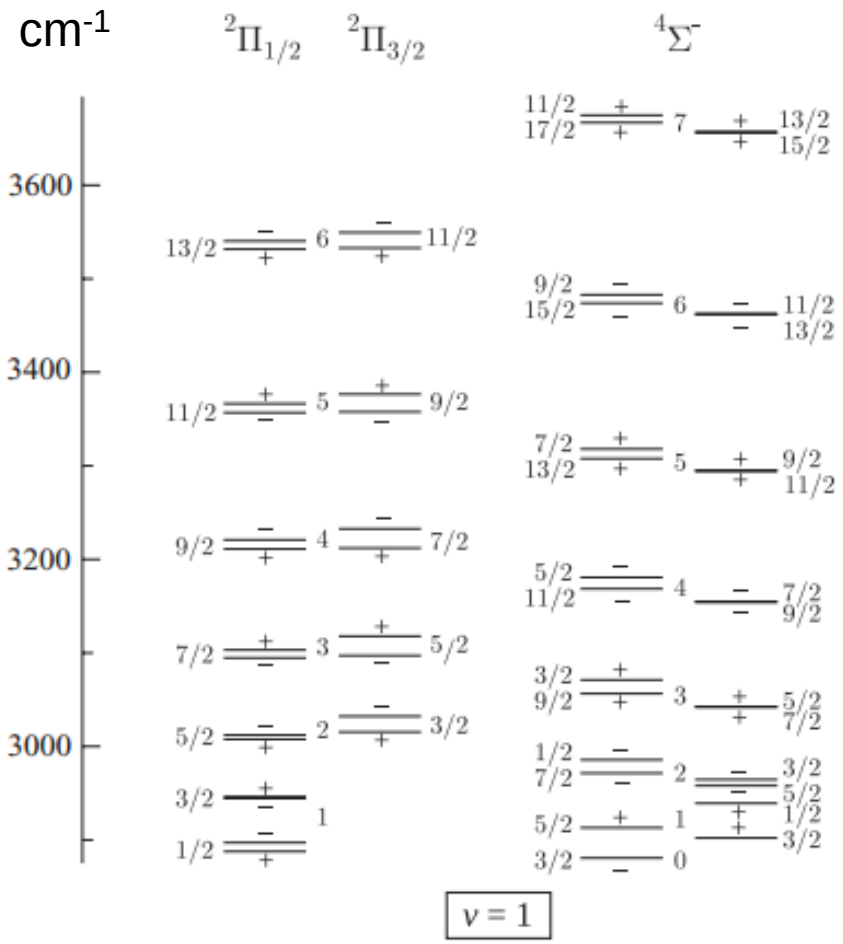
Frequencies & sensitivities of Λ-transitions in OH





Λ-doubling in NH^+. Perturbation from $^4\Sigma^-$ state



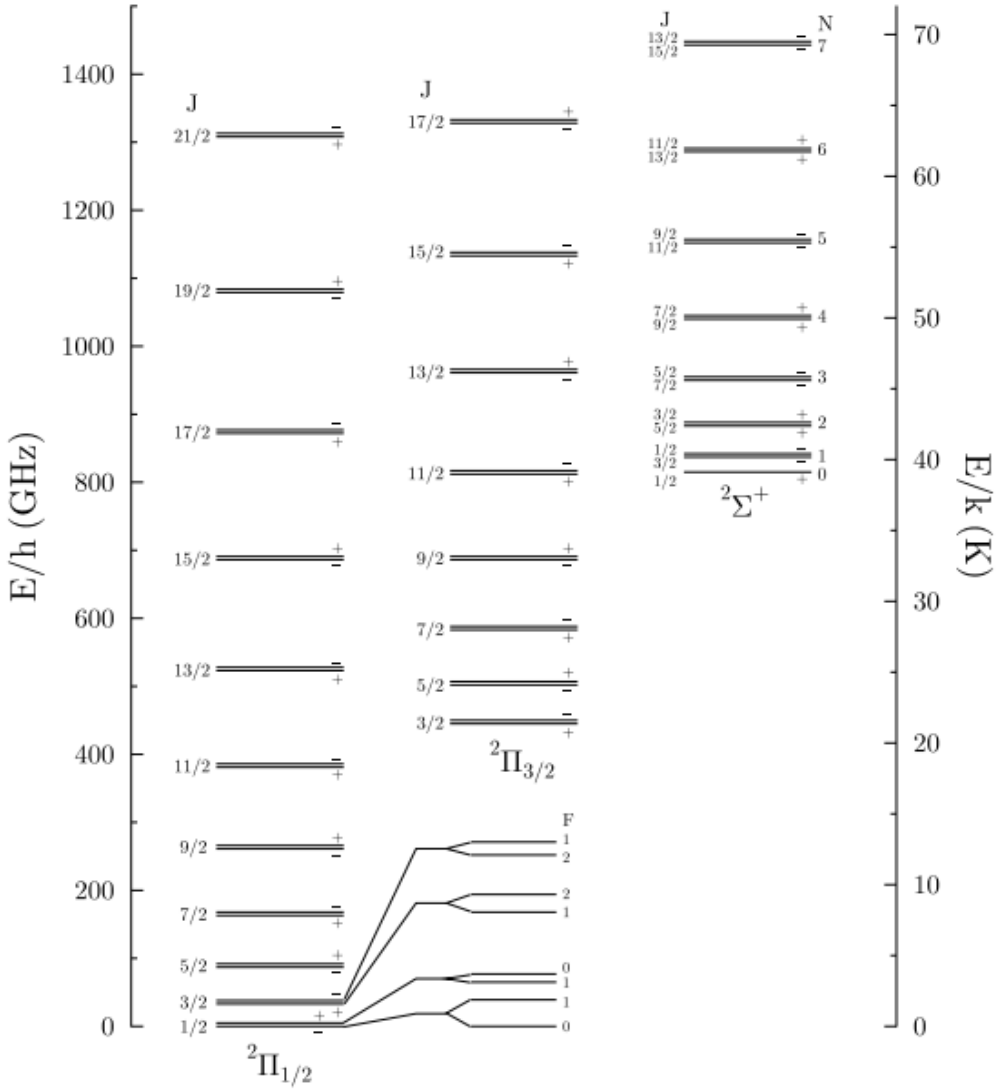


Sensitivity coefficients for NH^+

J^p	E_{up}	ω	Q_α	Q_μ
	Transitions for $^2\Pi_{3/2}, v = 0$			
$(3/2)^+$	105.405	0.244	−1.97	2.91
$(5/2)^-$	195.934	0.617	−1.02	2.34
$(7/2)^+$	317.542	1.082	−0.55	2.13
$(9/2)^-$	469.655	1.710	−0.02	2.73
$(11/2)^-$	655.253	3.410	19.71	−53.15
$(13/2)^-$	863.581	0.996	−11.10	−0.22
$(15/2)^+$	1103.851	0.150	−81.53	−126.86
$(17/2)^+$	1374.211	5.020	1.73	19.93
$(19/2)^+$	1694.241	20.595	3.65	−4.78
$(21/2)^-$	2017.566	15.979	2.66	−1.11
$(23/2)^+$	2373.114	15.516	2.01	0.32
$(25/2)^-$	2757.519	16.311	1.65	0.95
$(27/2)^+$	3169.622	17.721	1.43	1.29
$(29/2)^-$	3608.690	19.585	1.30	1.53

J^p	E_{up}	ω	Q_α	Q_μ
	Transitions for $^2\Pi_{3/2}, v = 1$			
$(3/2)^-$	151.564	16.803	1.86	−0.67
$(5/2)^+$	237.233	20.745	2.76	−1.79
$(7/2)^-$	352.021	20.618	3.41	−2.37
$(9/2)^+$	495.901	18.888	3.91	−2.72
$(11/2)^-$	668.781	16.511	4.36	−2.99
$(13/2)^+$	870.530	13.906	4.86	−3.27
$(15/2)^-$	1100.956	11.276	5.50	−3.64
$(17/2)^+$	1359.806	8.724	6.44	−4.25
$(19/2)^-$	1646.767	6.297	8.04	−5.39
$(21/2)^+$	1961.476	4.008	11.39	−7.90
$(23/2)^-$	2303.527	1.858	22.27	−16.23
$(25/2)^-$	2672.636	0.158	−239.61	185.81
$(27/2)^+$	3069.899	2.041	−17.09	14.15
$(29/2)^-$	3492.954	3.787	−8.62	7.58

Level structure of C_3H



Total angular momentum ***J*** includes vibrational angular momentum ***G***:

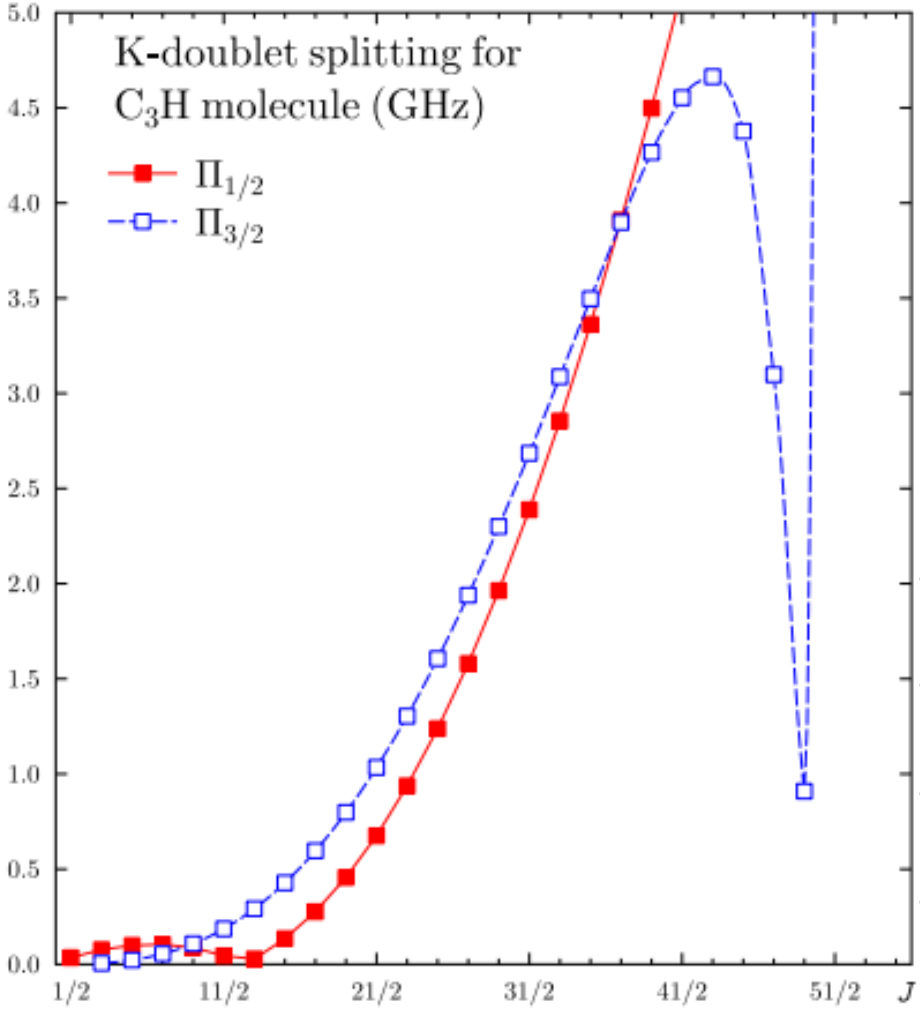
$$\boldsymbol{J} = \boldsymbol{N} + \boldsymbol{S} = \boldsymbol{R} + \boldsymbol{G} + \boldsymbol{L} + \boldsymbol{S}.$$

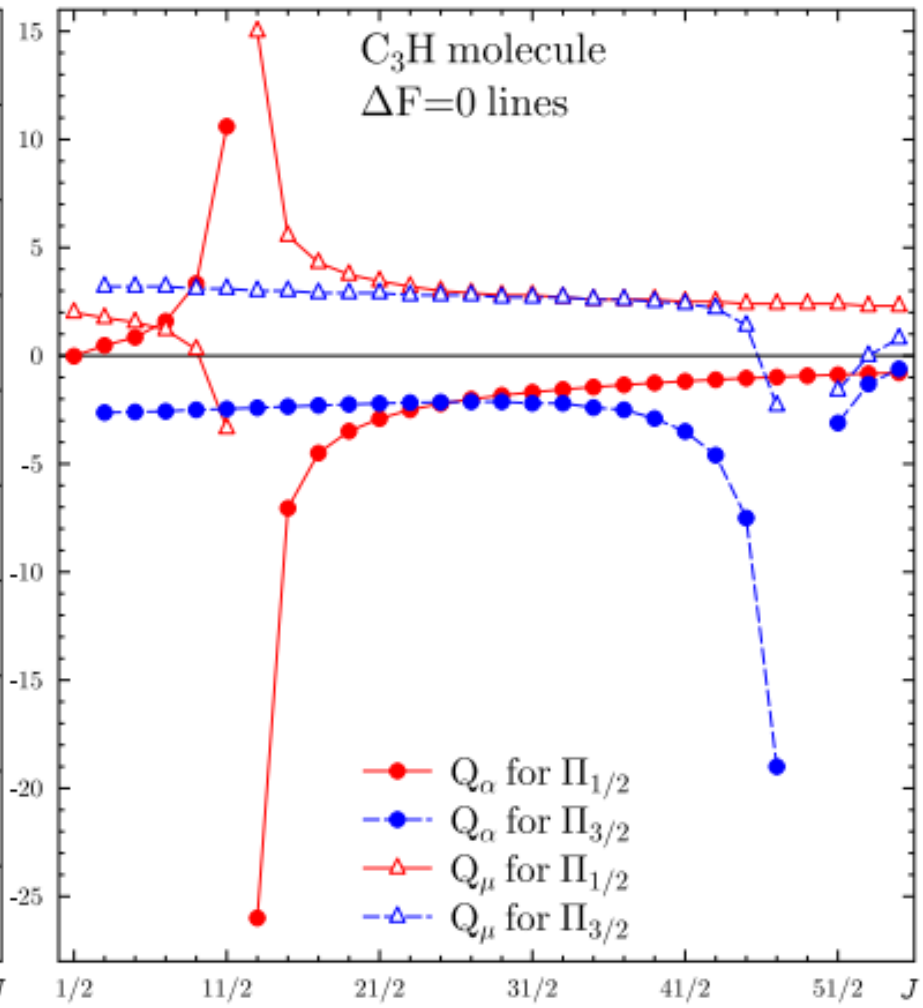
Projection of the angular momentum on the molecular axis is:

$$\Omega = K + \Sigma = l + \Lambda + \Sigma.$$

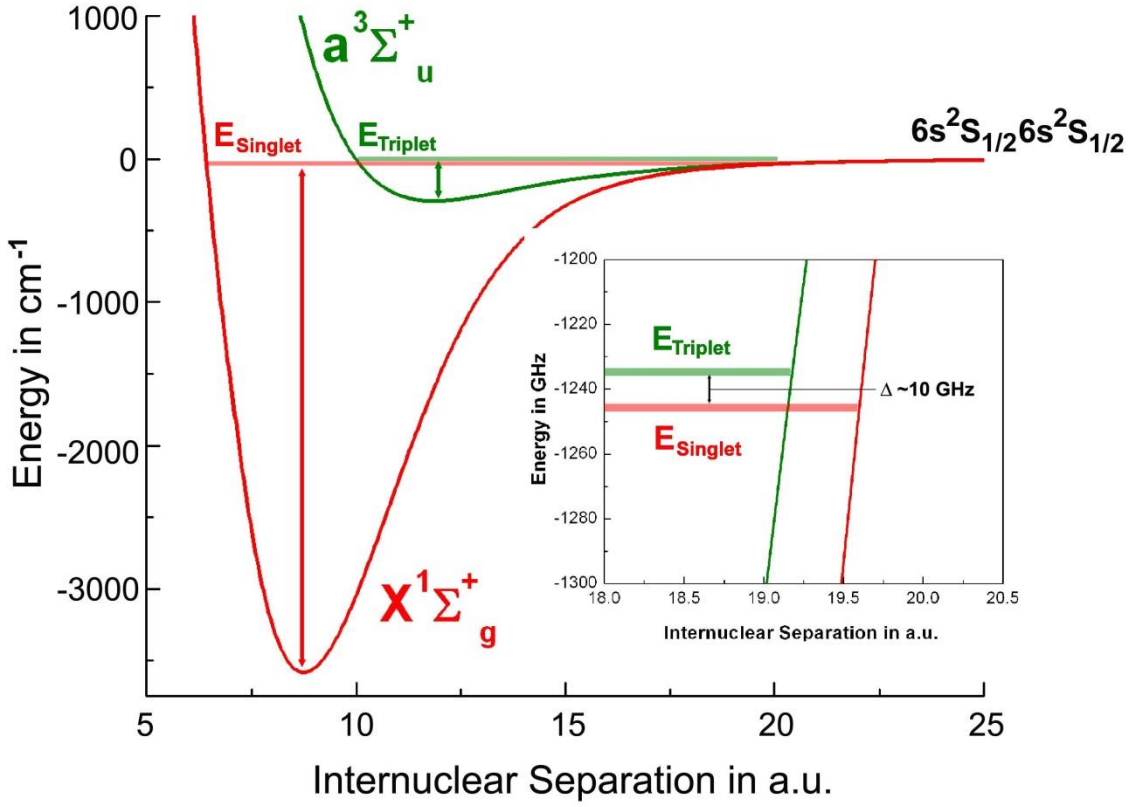
States with the same quantum number K strongly interact *(Renner-Teller effect)*.

Frequencies & sensitivities of *K*-transitions in C_3H





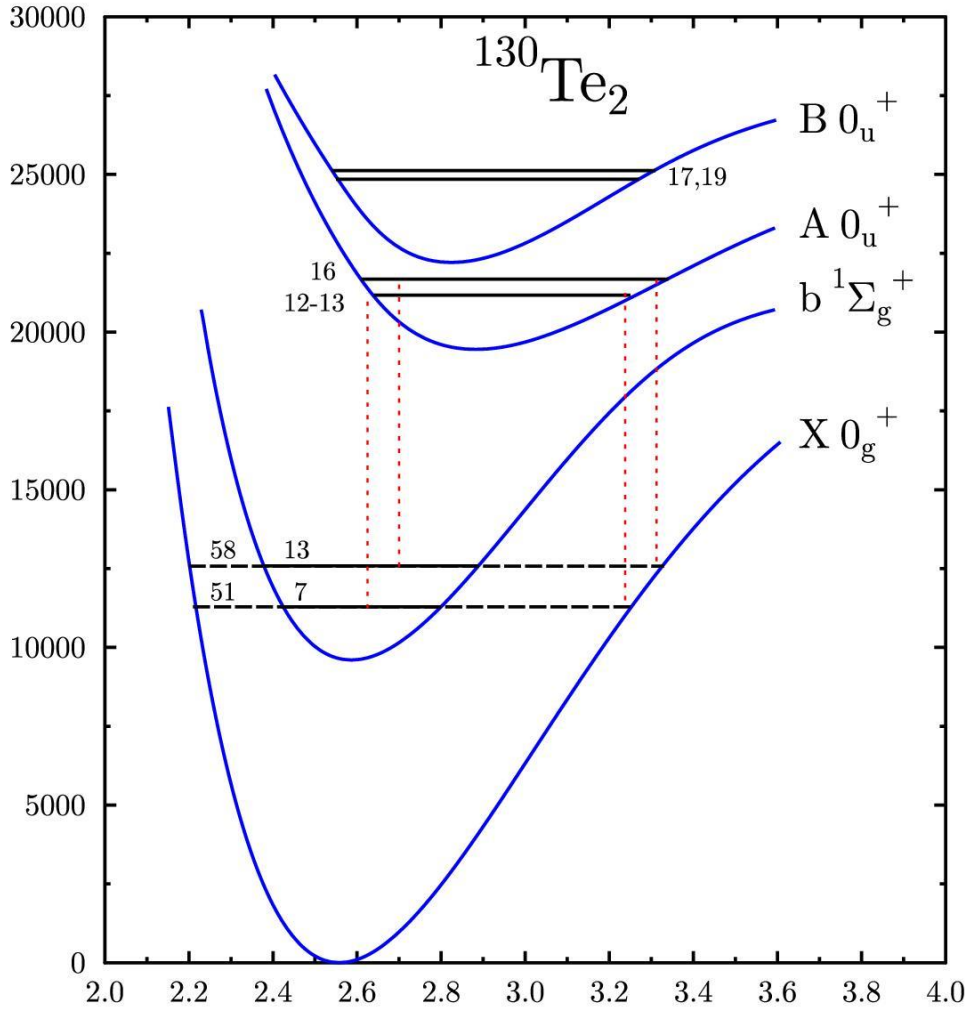
Matching electronic energy with vibrational ladder *(D DeMille)*



$^{137}Cs_2$

From Sainis, S, Ph.D. Thesis, Yale University, 2005

$^{130}Te_2$ *[D DeMille, S Kotochigova, & MK]*



Conclusions

- Dimensionless sensitivity coefficients correspond to the relative sensitivity to the VFC.
- “Low frequency” transitions between quasi degenerate states may have large dimensionless sensitivity coefficients.
- Both accidental and symmetry-induced degeneracy can lead to high relative sensitivity.
- High absolute sensitivity can be achieved when accidental degeneracy takes place at high energy scale (nuclei, HCI).
- Molecules provide us with many examples of high dimensionless sensitivities. High absolute sensitivity is much more rare.
- High relative sensitivity is very important for astrophysics where lines are Doppler-broadened.