Molecules and electronic, vibrational and rotational structure

Max Born
Nobel 1954

Robert Oppenheimer

Gerhard Herzberg
Nobel 1971

Hamiltonian for a molecule

$$H = -\frac{\hbar^2}{2m}\sum_i \nabla_i^2 - \sum_A \frac{\hbar^2}{2M_A}\nabla_A^2 + V\left(\vec{R},\vec{r}\right)$$

i refers to electrons, A to nuclei;
Potential energy terms:

$$V\left(\vec{R},\vec{r}\right) = -\sum_{A,i}\frac{Z_A e^2}{4\pi\varepsilon_0 r_{Ai}} + \sum_{A>B}\frac{Z_A Z_B e^2}{4\pi\varepsilon_0\left|R_A - R_B\right|} + \sum_{i>j}\frac{e^2}{4\pi\varepsilon_0 r_{ij}}$$

Assume that the wave function of the system is separable and can be written as:

$$\Psi_{\text{mol}}\left(\vec{r}_i,\vec{R}_A\right) = \psi_{\text{el}}\left(\vec{r}_i;\vec{R}\right)\chi_{\text{nuc}}\left(\vec{R}\right)$$

Assume that the electronic wave function $\psi_{\text{el}}\left(\vec{r}_i;\vec{R}\right)$ can be calculated for a particular R

Then: $\nabla_i^2\psi_{\text{el}}\left(\vec{r}_i;\vec{R}\right)\chi_{\text{nuc}}\left(\vec{R}\right) = \chi_{\text{nuc}}\left(\vec{R}\right)\nabla_i^2\psi_{\text{el}}\left(\vec{r}_i;\vec{R}\right)$

$$\nabla_A^2\psi_{\text{el}}\chi_{\text{nuc}} = \psi_{\text{el}}\nabla_A^2\chi_{\text{nuc}} + 2\left(\nabla_A\psi_{\text{el}}\right)\left(\nabla_A\chi_{\text{nuc}}\right) + \nabla_A^2\psi_{\text{el}}$$

Born-Oppenheimer: the derivative of electronic wave function w.r.t nuclear coordinates is small:

$$\nabla_A\psi_{\text{el}} \approx 0$$

Nuclei can be considered stationary.
Then:

$$\nabla_A^2\psi_{\text{el}}\chi_{\text{nuc}} = \psi_{\text{el}}\nabla_A^2\chi_{\text{nuc}}$$

Separation of variables is possible.

Insert results in the Schrödinger equation:

$$H_{\text{mol}}\psi_{\text{el}}\chi_{\text{nuc}} = E_{\text{mol}}\psi_{\text{el}}\chi_{\text{nuc}}$$

Separation of variables in the molecular Hamiltonian

$$H\Psi_{\mathrm{mol}} = \chi_{\mathrm{nuc}}\left\{-\frac{\hbar^2}{2m}\sum_i \nabla_i^2 + \sum_{i>j}\frac{e^2}{4\pi\varepsilon_0 r_{ij}} - \sum_{A,i}\frac{Z_A e^2}{4\pi\varepsilon_0 r_{Ai}}\right\}\psi_{\mathrm{el}} +$$

$$\psi_{\mathrm{el}}\left\{\sum_{A>B}\frac{Z_A Z_B e^2}{4\pi\varepsilon_0\left|R_A - R_B\right|} - \sum_A \frac{\hbar^2}{2M_A}\nabla_A^2\right\}\chi_{\mathrm{nuc}} = E_{\mathrm{total}}\Psi_{\mathrm{mol}}$$

The wave function for the electronic part can be written separately and "solved"; consider this as a problem of molecular binding.

$$\left\{-\frac{\hbar^2}{2m}\sum_i \nabla_i^2 + \sum_{i>j}\frac{e^2}{4\pi\varepsilon_0 r_{ij}} - \sum_{A,i}\frac{Z_A e^2}{4\pi\varepsilon_0 r_{Ai}}\right\}\psi_{\mathrm{el}}\left(\vec{r}_i;\vec{R}\right) = E_{\mathrm{el}}\psi_{\mathrm{el}}\left(\vec{r}_i;\vec{R}\right)$$

Solve the electronic problem for each R and insert result E_{el} in wave function.
This yields a wave equation for the nuclear motion:

$$\left\{-\sum_A \frac{\hbar^2}{2M_A}\nabla_A^2 + \sum_{A>B}\frac{Z_A Z_B e^2}{4\pi\varepsilon_0\left|R_A - R_B\right|} + E_{el}\left(\vec{R}\right)\right\}\chi_{\mathrm{nuc}} = E_{\mathrm{total}}\chi_{\mathrm{nuc}}$$

Schrodinger equation for the nuclear motion

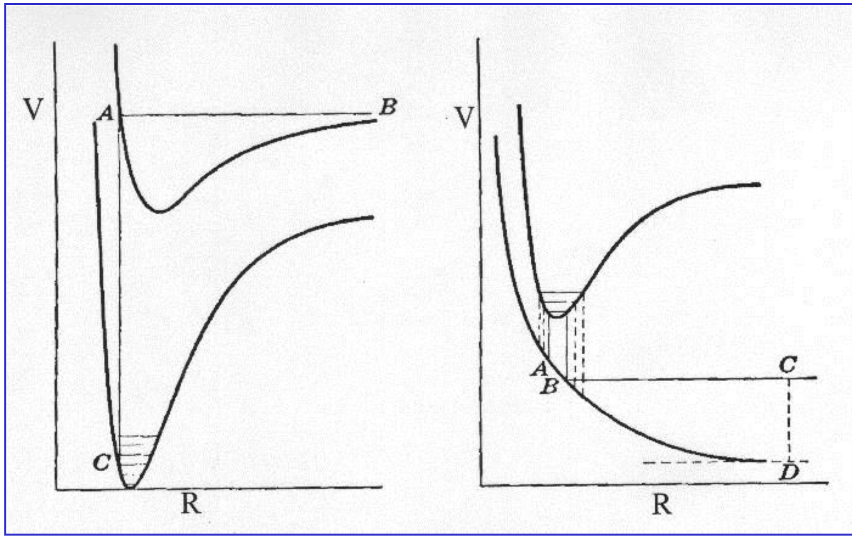
The previous analysis yields:

$$\left\{-\sum_{A}\frac{\hbar^2}{2M_A}\nabla_A^2+\sum_{A>B}\frac{Z_AZ_Be^2}{4\pi\varepsilon_0\left|R_A-R_B\right|}+E_{el}(\vec{R})\right\}\chi_{\text{nuc}}=E_{\text{total}}\chi_{\text{nuc}}$$

This is a Schrödinger equation with a potential energy:

$$V\left(\vec{R}\right)=\underbrace{\sum_{A>B}\frac{Z_AZ_Be^2}{4\pi\varepsilon_0\left|R_A-R_B\right|}}_{\text{nuclear repulsion}}+\underbrace{E_{\text{el}}\left(\vec{R}\right)}_{\text{chemical binding}}$$

Typical potential energy curves in molecules



Now try to find solutions to the Hamiltonian for the nuclear motion

$$-\sum_{A}\frac{\hbar^2}{2M_A}\nabla_A^2\chi_{\text{nuc}}\left(\vec{R}\right)+V(\vec{R})\chi_{\text{nuc}}\left(\vec{R}\right)=E\chi_{\text{nuc}}\left(\vec{R}\right)$$

Quantized motion in a diatomic molecule

Quantummechanical two-particle problem
Transfer to centre-of-mass system

$$\mu = \frac{M_A M_B}{M_A + M_B}$$

Single-particle Schrödinger equation

$$-\frac{\hbar^2}{2\mu}\Delta_{\vec{R}}\chi_{\text{nuc}}\left(\vec{R}\right)+V(\vec{R})\chi_{\text{nuc}}\left(\vec{R}\right)=E\chi_{\text{nuc}}\left(\vec{R}\right)$$

Consider the similarity and differences between this equation and that of the H-atom:
- interpretation of the wave function
- shape of the potential

Laplacian:

$$\Delta_{\vec{R}} = \frac{1}{R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial}{\partial R}\right)$$

$$+\frac{1}{R^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{R^2\sin\theta}\frac{\partial^2}{\partial\phi^2}$$

Angular part is the well-know equation with solutions:

Angular momentum operators

Spherical harmonic wave functions !

Angular momentum in a molecule

Solution:

$$\vec{N}^2 \left| N, M \right\rangle = \hbar^2 N(N+1) \left| N, M \right\rangle$$

$$N_z \left| N, M \right\rangle = \hbar M \left| N, M \right\rangle$$

with

$$N = 0,1,2,3\ldots$$

$$M = -N, -N+1, \ldots, N$$

And angular wave function

$$\left| N, M \right\rangle = Y_{NM}(\theta, \phi)$$

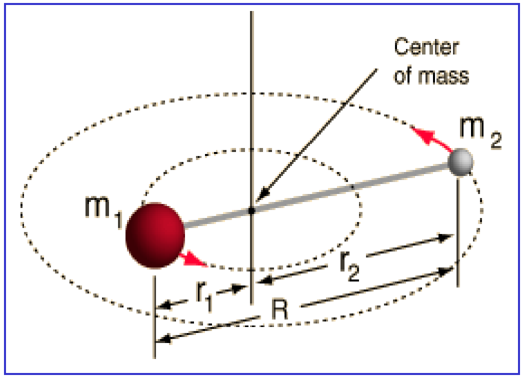
Hence the wave function of the molecule:

$$\chi_{\mathrm{nuc}}(R, \theta, \phi) = \Xi(R) Y_{NM}(\theta, \phi)$$

Reduction of molecular Schrödinger equation

$$\left[-\frac{\hbar^2}{2\mu R^2} \frac{\partial}{\partial R}\left(R^2 \frac{\partial}{\partial R} \right) + \frac{1}{2\mu R^2} \vec{N}^2 + V(R) \right] \chi_{\mathrm{nuc}}(R) = E_{\mathrm{vib,rot}} \chi_{\mathrm{nuc}}(R)$$

Eigenenergies of a "Rigid Rotor"



Rigid rotor, so it is assumed that $R = R_e = \text{constant}$

Choose: $V(R) = V(R_e) = 0$

All derivates $\frac{\partial}{\partial R}$ yield zero

Insert in:

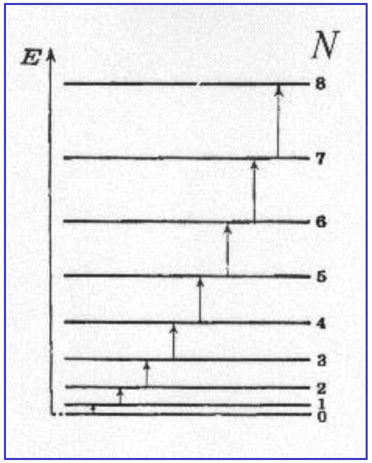
$$\left[-\frac{\hbar^2}{2\mu R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial}{\partial R}\right)+\frac{1}{2\mu R^2}\vec{N}^2+V(R)\right]\chi_{\text{nuc}}(R)=E_{\text{vib,rot}}\chi_{\text{nuc}}(R)$$

$$\left[\frac{1}{2\mu R_e^2}\vec{N}^2\right]\chi_{\text{nuc}}(R)=E_{\text{vib,rot}}\chi_{\text{nuc}}(R)$$

So quantized motion of rotation: $E_{\text{rot}} = \hbar^2\frac{N(N+1)}{2\mu R_e^2} = BN(N+1)$

With B the rotational constant

isotope effect



→ Deduce R_e from spectroscopy

Vibrational motion

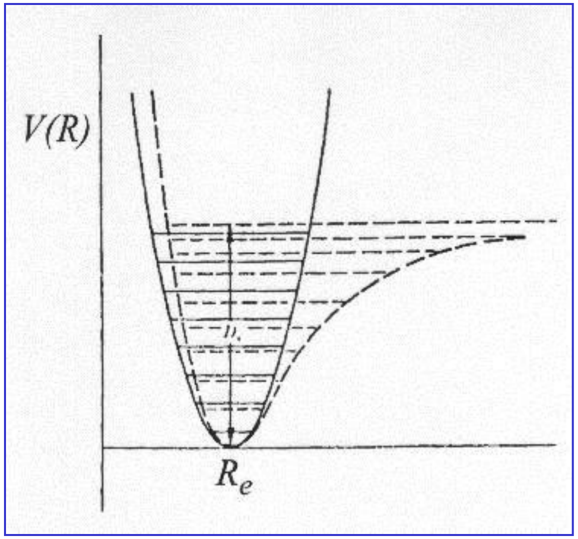
$$\left[-\frac{\hbar^2}{2\mu R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial}{\partial R}\right)+\frac{1}{2\mu R^2}\vec{N}^2+V(R)\right]\chi_{\text{nuc}}(R)=E_{\text{vib,rot}}\chi_{\text{nuc}}(R)$$

Non-rotation: $N=0$

Insert : $\Xi(R)=\frac{Q(R)}{R}$

→

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2}+V(R)\right]Q(R)=E_{\text{vib}}Q(R)$$



Make a Taylor series expansion around $\rho=R-R_e$

$$V(R)=V(R_e)+\left.\frac{dV}{dR}\right|_{R_e}\rho+\frac{1}{2}\left.\frac{d^2V}{dR^2}\right|_{R_e}\rho^2+\ldots$$

$V(R_e)=0$ by choice

$\left.\frac{dV}{dR}\right|_{R_e}=0$ at the bottom of the well

Hence: $V(R)=k(R-R_e)^2$ harmonic potential

Vibrational motion

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{d\rho^2}+\frac{1}{2}k\rho^2\right]Q(\rho)=E_{\mathrm{vib}}Q(\rho)$$

So the wave function of a vibrating molecule resembles the 1-dimensional harmonic oscillator, solutions:

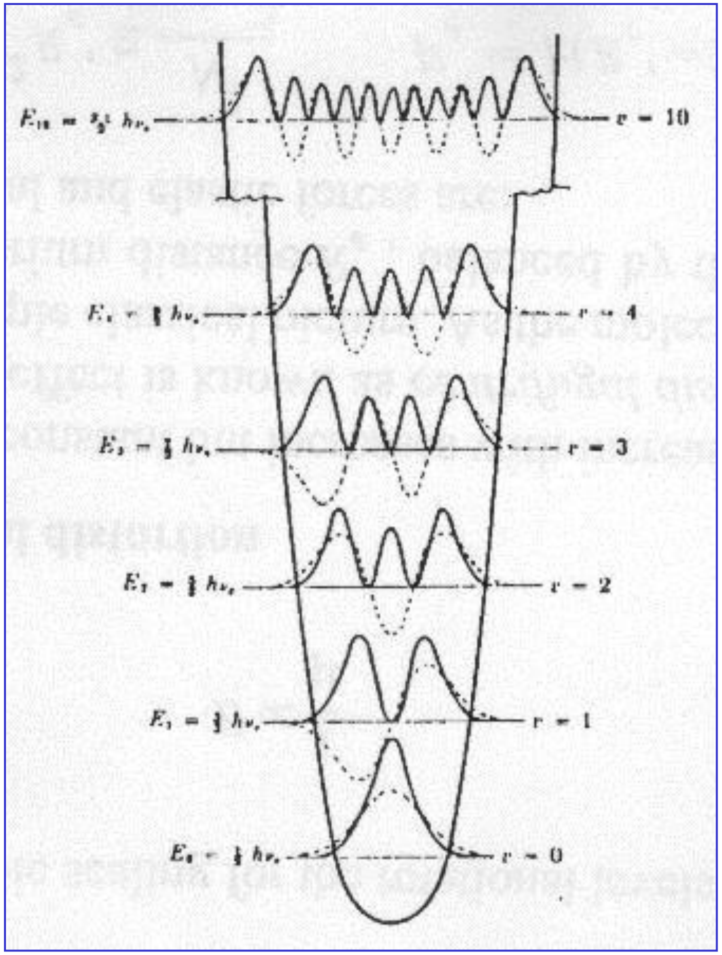
$$Q_v(\rho)=\frac{2^{v/2}\alpha^{1/4}}{\sqrt{v!}\,\pi^{1/4}}\exp\left[\frac{1}{2}\alpha\rho^2\right]H_v\left(\sqrt{\alpha}\,\rho\right)$$

with: $\alpha=\dfrac{\mu\omega_e}{\hbar}$ and $\omega_e=\sqrt{\dfrac{k}{\mu}}$

Energy eigenvalues:

$$E_{\mathrm{vib}}=\hbar\omega_e\left(v+\frac{1}{2}\right)=\hbar\sqrt{\frac{k}{\mu}}\left(v+\frac{1}{2}\right)$$

isotope effect



Finer details of the rovibrational motion

Centrifugal distortion:

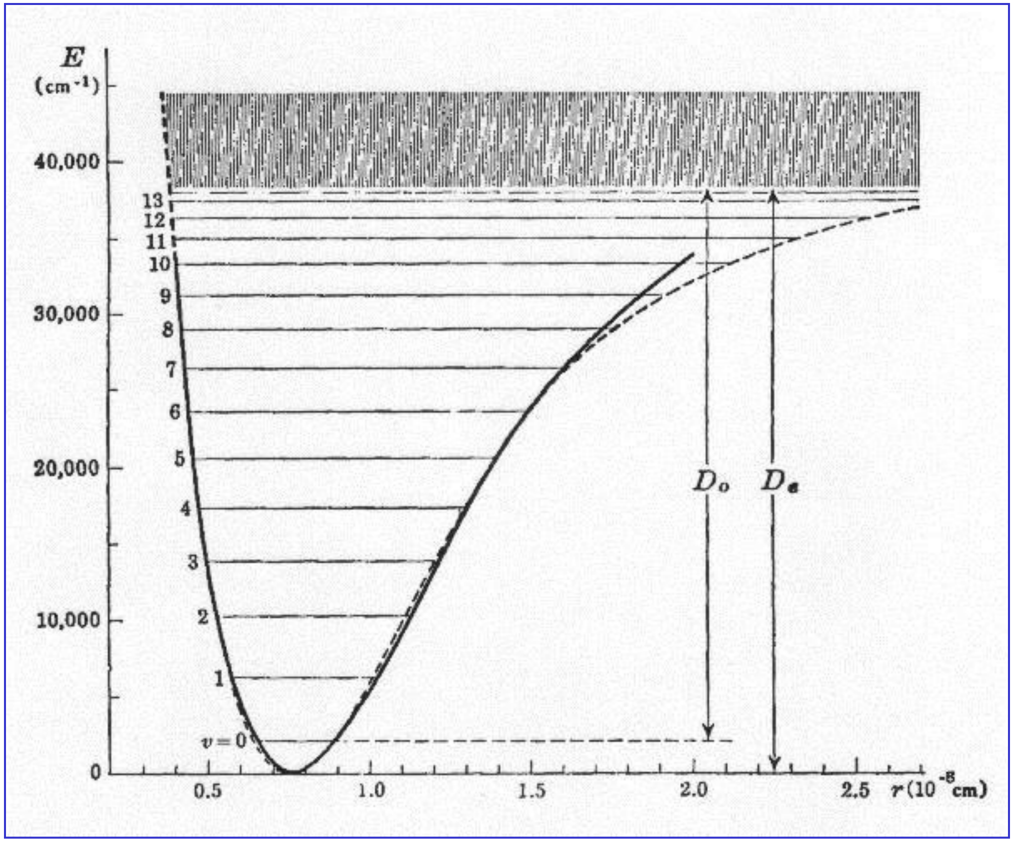
$$E_{\mathrm{rot}} = BN(N+1) - DN^2(N+1)^2$$

Anharmonic vibrational motion

$$E_{\mathrm{vib}} = \omega_e\left(v+\frac{1}{2}\right) - \omega_e x_e\left(v+\frac{1}{2}\right)^2 + \ldots$$

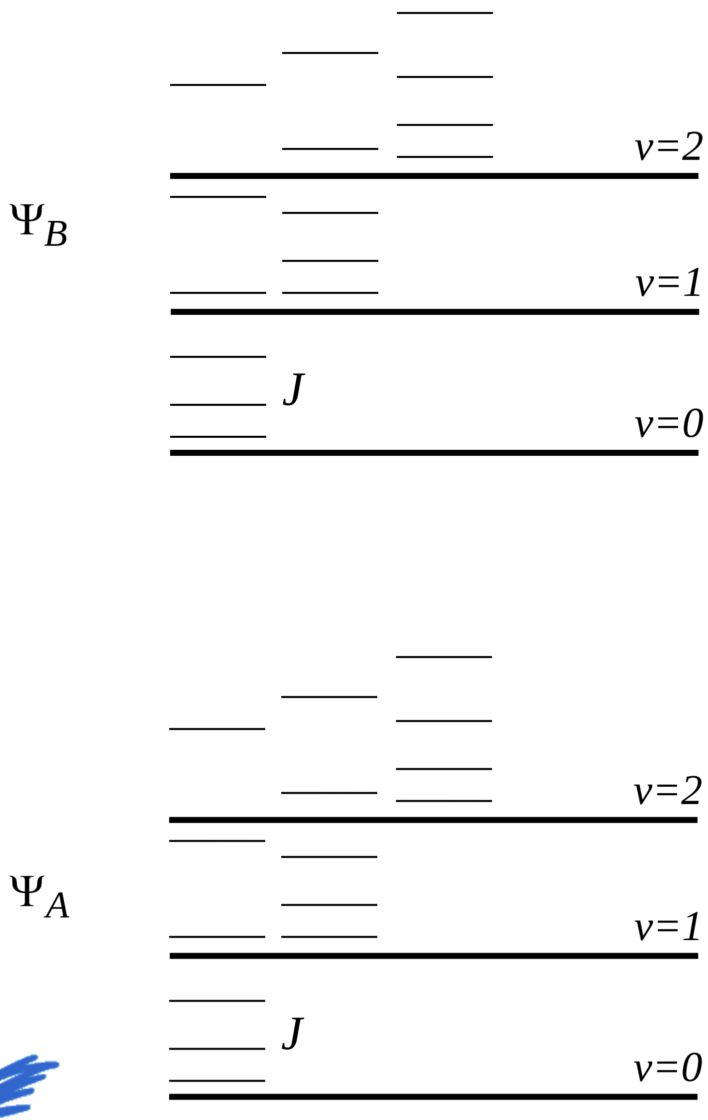
Dunham expansion:

$$E_{vN} = \sum_{k,l} Y_{kl}\left(v+\frac{1}{2}\right)^k N^l (N+1)^1$$



Vibrational energies in the H_2-molecule

Energy levels in a molecule: general structure



Rovibrational structure superimposed on electronic structure

Radiative transitions in molecules

The dipole moment in a molecule:

$$\mu = \mu_e + \mu_N = -\sum_i e\vec{r}_i + \sum_A eZ_A\vec{R}_A$$

In a molecule, there may be a:
- permanent or rotational dipole moment
- vibrational dipole moment

$$\vec{\mu}_N = \vec{\mu}_0 + \left(\frac{d}{dR}\vec{\mu}\right)_{R_e}\rho + \frac{1}{2}\left(\frac{d^2}{dR^2}\vec{\mu}\right)\rho^2$$

In atoms only electronic transitions, in molecules transitions within electronic state

Note for transitions: Einstein coefficient

$$B = \frac{\pi e^2}{3\varepsilon_0\hbar^2}\left|\mu_{ij}\right|^2$$

$$\Psi_{\text{mol}}\left(\vec{r}_i, \vec{R}_A\right) = \psi_{\text{el}}\left(\vec{r}_i; \vec{R}\right)\psi_{\text{vib}}\left(\vec{R}\right)$$

Dipole transition between two states

$$\mu_{if} = \int \Psi' \mu \Psi'' d\tau$$

Two different types of transitions

$$\mu_{if} = \int \psi'_{\text{el}}\psi'_{\text{vib}}\left(\mu_e + \mu_N\right)\psi''_{\text{el}}\psi''_{\text{vib}}d\tau =$$

$$\int\left(\int \psi'_{\text{el}}\mu_e\psi''_{\text{el}}d\vec{r}\right)\psi'_{\text{vib}}\psi''_{\text{vib}}d\vec{R} +$$

$$\int \psi'_{\text{el}}\psi''_{\text{el}}d\vec{r}\int \psi'_{\text{vib}}\mu_N\psi''_{\text{vib}}d\vec{R}$$

Electronic transitions

Rovibrational transitions

The Franck-Condon principle for electronic transitions in molecules

1st term:

$$\mu_{if} = \int \left(\int \psi'_{\mathrm{el}} \mu_e \psi''_{\mathrm{el}} d\vec{r} \right) \psi'_{\mathrm{vib}} \psi''_{\mathrm{vib}} d\vec{R}$$

Only contributions if (parity selection rule)

$$\psi'_{\mathrm{el}} \neq \psi''_{\mathrm{el}}$$

Franck-Condon approximation:
The electronic dipole moment independent of internuclear separation:

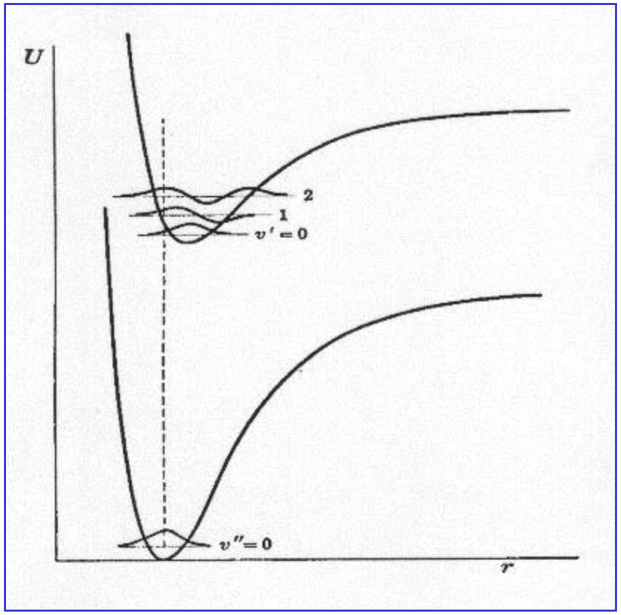
$$\overline{M}_e(R) = \int \psi'_{\mathrm{el}} \mu_e \psi''_{\mathrm{el}} d\vec{r}$$

Hence

$$\mu_{if} = \overline{M}_e(R) \int \psi'_{\mathrm{vib}} \psi''_{\mathrm{vib}} d\vec{R}$$

Intensity of electronic transitions

$$I \propto \left|\mu_{if}\right|^2 \propto \left| \int \psi'_{\mathrm{vib}} \psi''_{\mathrm{vib}} d\vec{R} \right|^2 \propto \geq \left| \langle v' | v'' \rangle \right|^2$$



Intensity proportional to the square of the wave function overlap

Rotational transitions in molecules

2nd term in the transition dipole

$$\mu_{if} = \langle \Psi_{N'M'} | \mu | \Psi_{NM} \rangle$$

Projection of the dipole moment vector on the quantization axis.
For rotation take the permanent dipole.

$$\vec{\mu} = \mu_0 \begin{bmatrix} \sin\theta\cos\phi \\ \sin\theta\sin\phi \\ \cos\theta \end{bmatrix} \propto \mu_0 Y_{1m}$$

$$\mu_{if} \propto \mu_0 \int\int Y_{N'M'} Y_{1m} Y_{NM} \, d\Omega$$

$$\propto \begin{pmatrix} N' & 1 & N \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} N' & 1 & N \\ M' & m & M \end{pmatrix}$$

$\longrightarrow$ Selection rules

$$\Delta N = \pm 1$$

$$\Delta M = 0, \pm 1$$

Purely rotational spectra

Level energies:

$$F_v = B_v N(N+1) - D_v N^2 (N+1)^2$$

Transition frequencies:

$$\nu = F_v(N') - F_v(N'') =$$
$$B_v[N'(N'+1) - N''(N''+1)]$$
$$- D_v\left[N'^2(N'+1)^2 - N''^2(N''+1)^2\right]$$

Ground state with *N''* and excited *N'*
Absorption in rotational ladder: *N'=N''+1*

$$\nu_{abs} = \underline{2B_v(N''+1)} - 4D_v(N''+1)^3$$

spacing between lines ~ *2B*

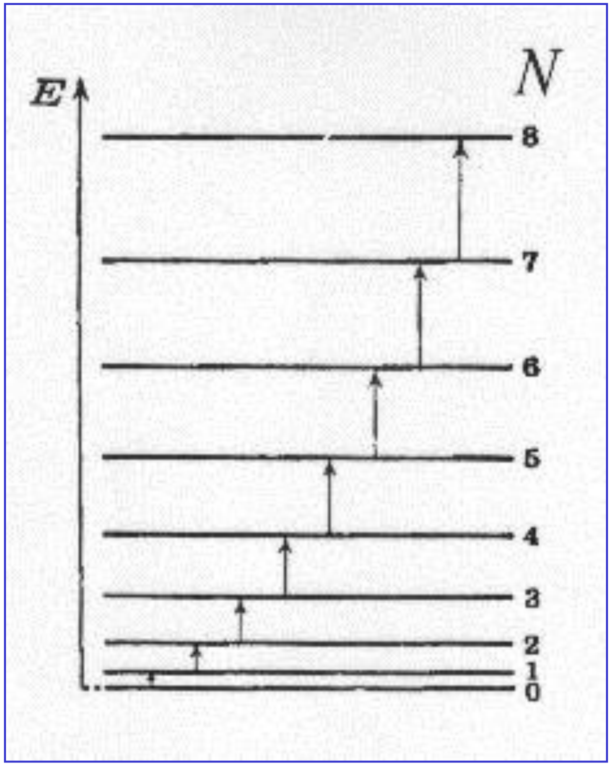
Rotational spectrum in a diatomic molecule

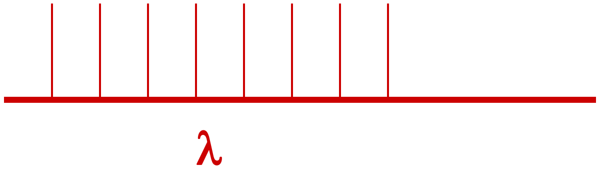
Ground state with N'' and excited N'
Absorption in rotational ladder: $N'=N''+1$

$$\nu_{\text{abs}} = \underline{2B_v(N''+1)} - 4D_v(N''+1)^3$$

spacing between lines ~ $2B$

In an absorption spectrum: R-lines
In an emission spectrum: P-lines





Homonuclear molecule

$$\mu_N = \sum_A eZ_A\vec{R}_A = eZ_A(\vec{R}_A - \vec{R}_A) = 0$$

For permanent dipole
No rotational spectrum

Vibrational transitions in molecules

2nd term in the transition dipole

$$\mu_{if} = \int \psi'_{\mathrm{el}}\psi''_{\mathrm{el}}\, d\vec{r} \int \psi'_{\mathrm{vib}}\mu_N \psi''_{\mathrm{vib}}\, d\vec{R}$$

Within a certain electronic state:

$$\psi'_{\mathrm{el}} = \psi''_{\mathrm{el}} \longrightarrow \int \psi'_{\mathrm{el}}\psi''_{\mathrm{el}}\, d\vec{r} = 1$$

Line intensity:

$$\mu_{if} = \langle v' | \mu_{\mathrm{vib}} | v'' \rangle$$

Permanent and induced dipole moments;

$$\vec{\mu}_N = \vec{\mu}_0 + \left(\frac{d}{dR}\vec{\mu} \right)_{R_e} \rho + \frac{1}{2}\left(\frac{d^2}{dR^2}\vec{\mu} \right)\rho^2$$

Permanent dipole does not produce a vibrational spectrum

$$\mu_{if} = \langle v' | \mu_0 | v'' \rangle = \mu_0 \langle v' | v'' \rangle = 0$$

Wave functions for one electronic state are orthogonal.

$$\mu_{if} = \langle v' | \left(\frac{d}{dR}\vec{\mu} \right)_{R_e} \rho | v'' \rangle \propto \langle v' | \rho | v'' \rangle$$

Dipole moment should vary with
Displacement → vibrational spectrum

Vibrational transitions in molecules

Permanent and induced dipole moments;

$$\mu_{if} = \langle v' | \mu_{\mathrm{vib}} | v'' \rangle = \langle v' | a\rho + b\rho^2 | v'' \rangle$$

First order: the vibrating dipole moment

$$\mu_{if} = \langle v' | \mu_{\mathrm{vib}} | v'' \rangle \propto \langle v' | \rho | v'' \rangle$$

Homonuclear molecule

$$\mu_N = \sum_A eZ_A \vec{R}_A = eZ_A(\vec{R}_A - \vec{R}_A) = 0$$

For all derivatives
No vibrational dipole spectrum

In the harmonic oscillator approximation;

$$\langle n | \rho | k \rangle = \int Q_n(\rho)\rho Q_k(\rho)d\rho = \sqrt{\frac{\hbar}{\mu\omega}}\left[\sqrt{\frac{n}{2}}\delta_{k,n-1} + \sqrt{\frac{n+1}{2}}\delta_{k,n+1}\right]$$

Selection rules: $\Delta v = v' - v = \pm 1$

Higher order transitions (overtones) from:

- anharmonicity in potential
- induced dipole moments

Rovibrational spectra in a diatomic molecule

Level energies:

$$T = G(v) + F_v(N)$$

with:

$$F_v = B_v N(N+1) - D_v N^2 (N+1)^2$$

$$G(v) = \omega_e \left(v + \frac{1}{2} \right) - \omega_e x_e \left(v + \frac{1}{2} \right)^2$$

Transitions from

v'' (ground) to v' (excited)

$$\sigma(v'-v'') = \sigma_0 + F_{v'}(N') - F_{v''}(N'')$$

with

$$\sigma_0 = G(v') - G(v'')$$

the band origin; the rotationless transition (not always visible)

Transitions

R-branch ($N'=N''+1$) – neglect D

$$\sigma_R = \sigma_0 + 2B_{v'} + (3B_{v'} - B_{v''})N + (B_{v'} - B_{v''})N^2$$

For $B_{v'} = B_{v''}$

$$\sigma_R = \sigma_0 + 2B_{v'}(N+1)$$

P-branch ($N'=N''$-1) – neglect D

$$\sigma_P = \sigma_0 - (B_{v'} + B_{v''})N + (B_{v'} - B_{v''})N^2$$

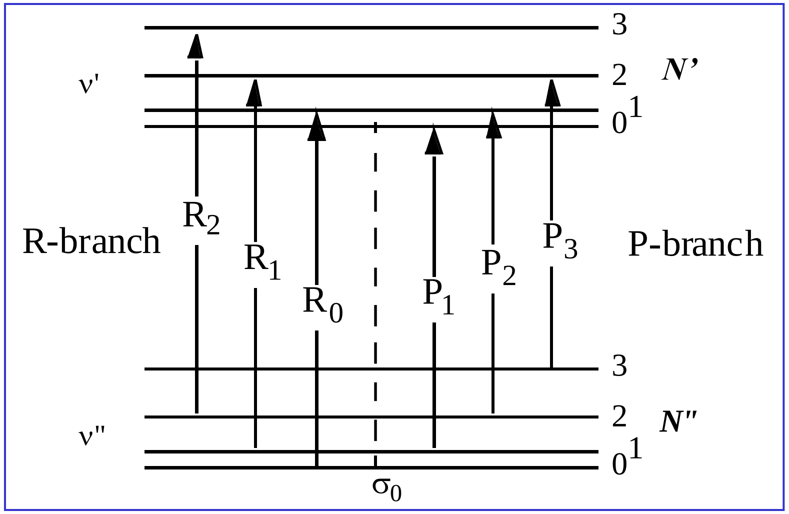
For $B_{v'} = B_{v''}$

$$\sigma_R = \sigma_0 + 2B_{v'}(N+1)$$

Rovibrational spectra

$$\sigma_R = \sigma_0 + 2B_{v'} + (3B_{v'} - B_{v''})N + (B_{v'} - B_{v''})N^2$$

$$\sigma_P = \sigma_0 - (B_{v'} + B_{v''})N + (B_{v'} - B_{v''})N^2$$



More precisely spacing between lines:

$$\sigma_R(N+1) - \sigma_R(N) \approx 3B_{v'} - B_{v''} < 2B_{v'}$$

$$\sigma_P(N+1) - \sigma_P(N) \approx B_{v'} + B_{v''} > 2B_{v'}$$

If, as usual: $B_{v'} < B_{v''}$

Rotational constant in excited state is smaller.

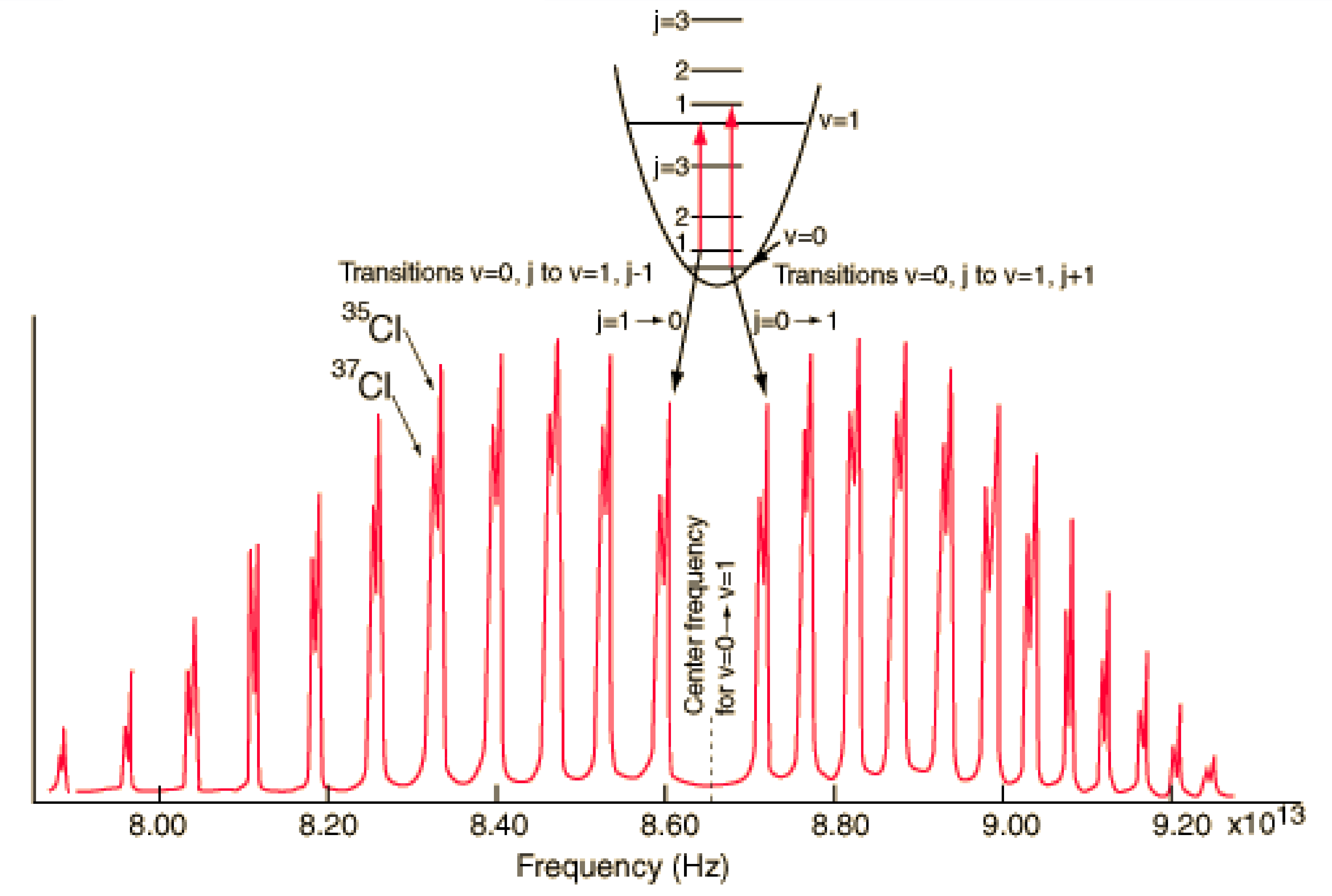
→

Spacing in P branch is larger
Band head formation in R-branch

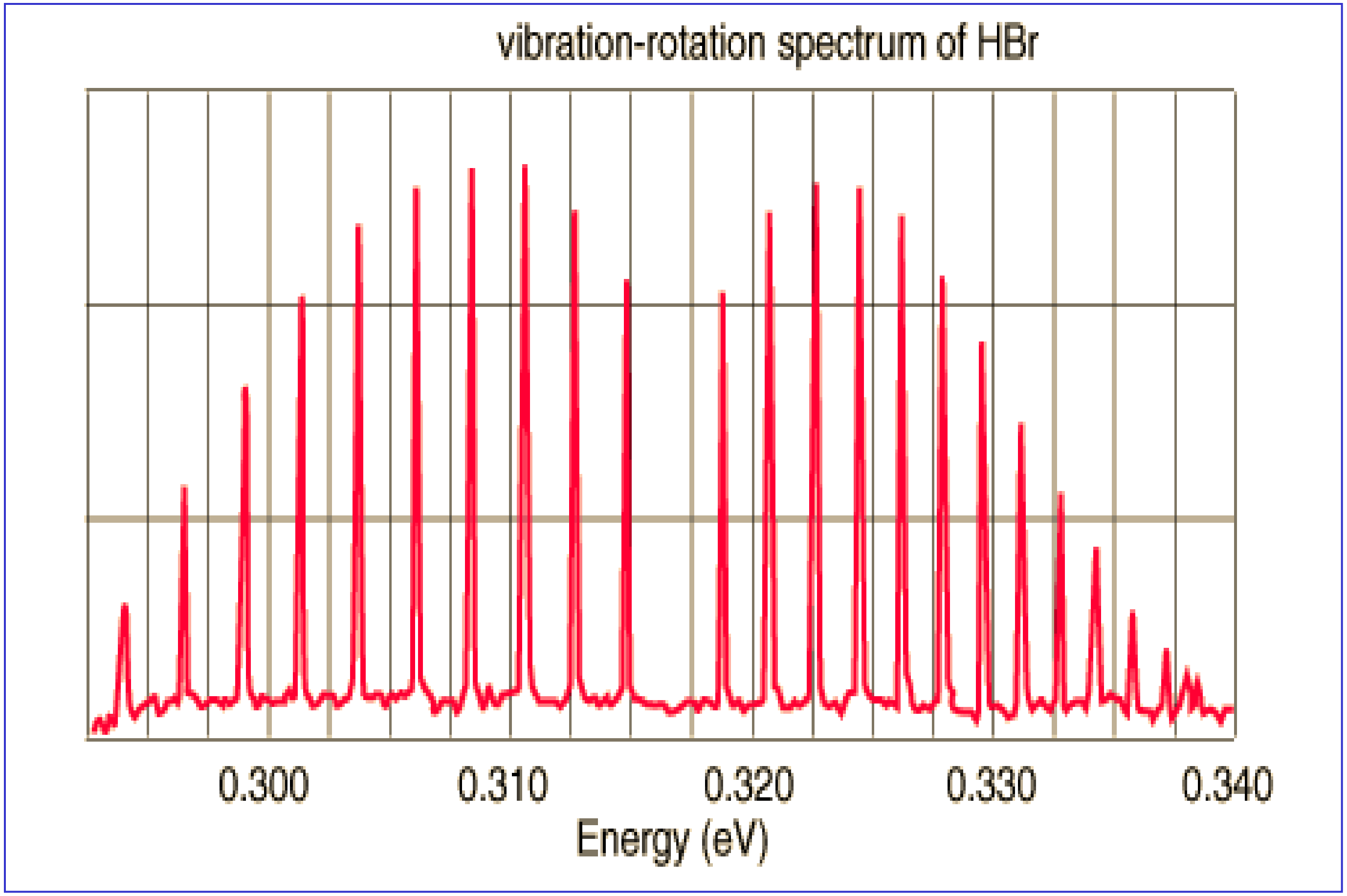
Spacing between R(0) and P(1) is $4B$

"band gap"

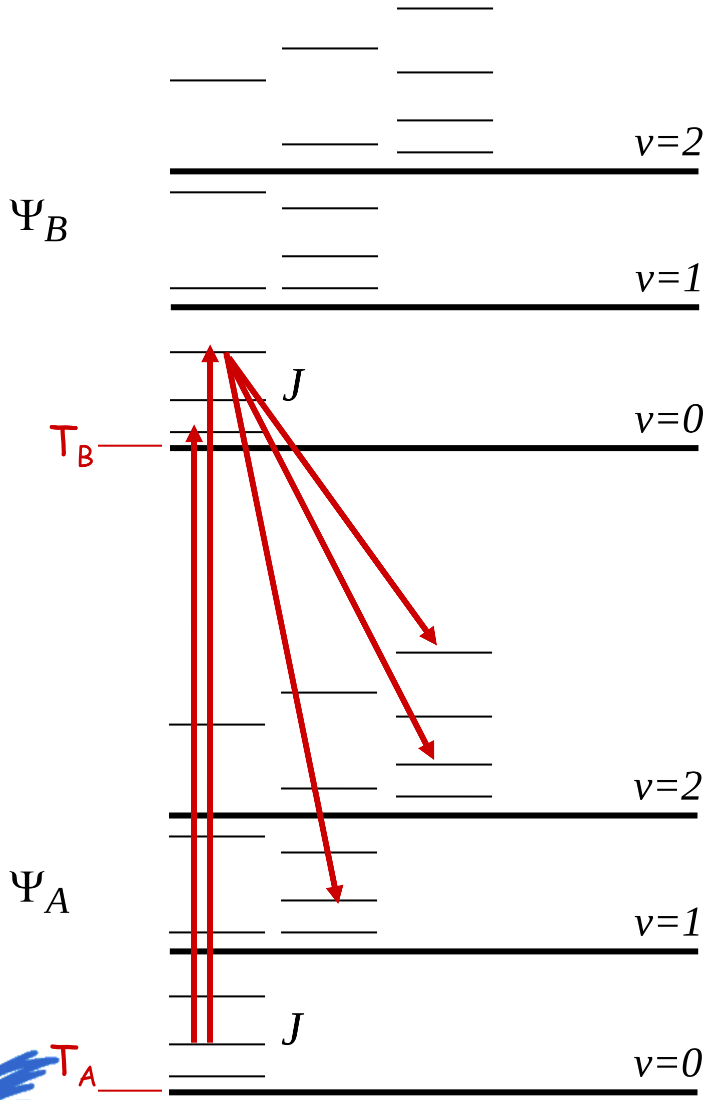
Example: rovibrational spectrum of HCl; fundamental vibration



Example: rovibrational spectrum of HBr; fundamental vibration



Rovibronic spectra



Vibrations → governed by the Franck-Condon principle

Rotations → governed by angular momentum selection rules

Transition frequencies

$$\nu = T' - T''$$

$$T' = T_B + G'(v') + F_v'(N')$$

$$T'' = T_A + G''(v'') + F_v''(N'')$$

R and P branches can be defined in the same way

$$\sigma_R = \sigma_0 + 2B_{v'} + (3B_{v'} - B_{v''})N + (B_{v'} - B_{v''})N^2$$

$$\sigma_P = \sigma_0 - (B_{v'} + B_{v''})N + (B_{v'} - B_{v''})N^2$$

Band head structures and Fortrat diagram

$$\sigma_R = \sigma_0 + 2B_{v'} + (3B_{v'} - B_{v''})N + (B_{v'} - B_{v''})N^2$$

$$\sigma_P = \sigma_0 - (B_{v'} + B_{v''})N + (B_{v'} - B_{v''})N^2$$

Define:

$m = N + 1$ for the R-branch

$m = -N$ for the P-branch

then for both branches:

$$\sigma = \sigma_0 + (B_{v'} + B_{v''})m + (B_{v'} - B_{v''})m^2$$

if: $B_{v'} < B_{v''}$

$$\sigma = \sigma_0 + \alpha m - \beta m^2$$

A parabola represents both branches

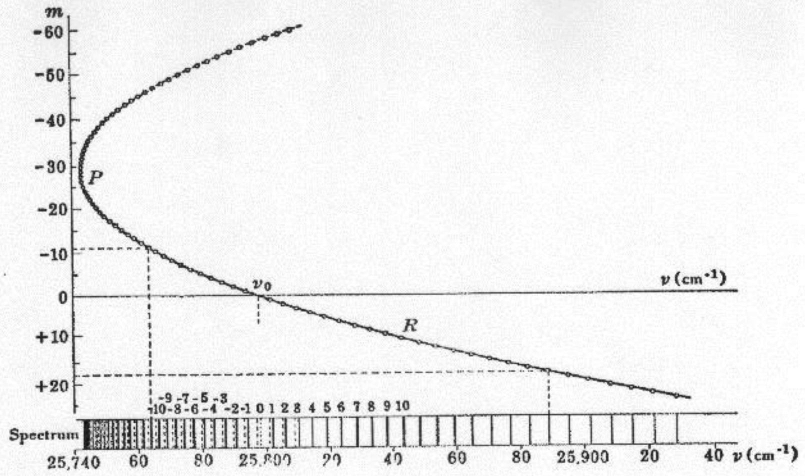


FIG. 24. **Fortrat Parabola of the CN Band 3883 Å (see Fig. 18).** The schematic spectrum below is drawn to the same scale as the Fortrat parabola above. The relation between curve and spectrum is indicated by broken lines for two points ($m = -11$ and $m = +18$). No line is observed at $m = 0$ (dotted line).

- no line for $m=0$; band gap
- there is always a band head, in one branch

Population distributions; vibrations

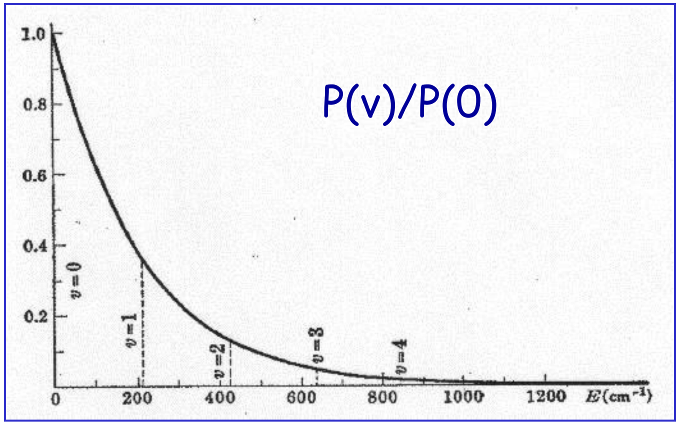
Probability of finding a molecule in a vibrational quantum state:

$$P(v) = \frac{e^{-E(v)/kT}}{\sum_{v} e^{-E(v)/kT}}$$

$$= \frac{1}{Z} e^{\frac{-\omega_e (v+1/2)}{kT}}$$

→

Boltzmann distribution



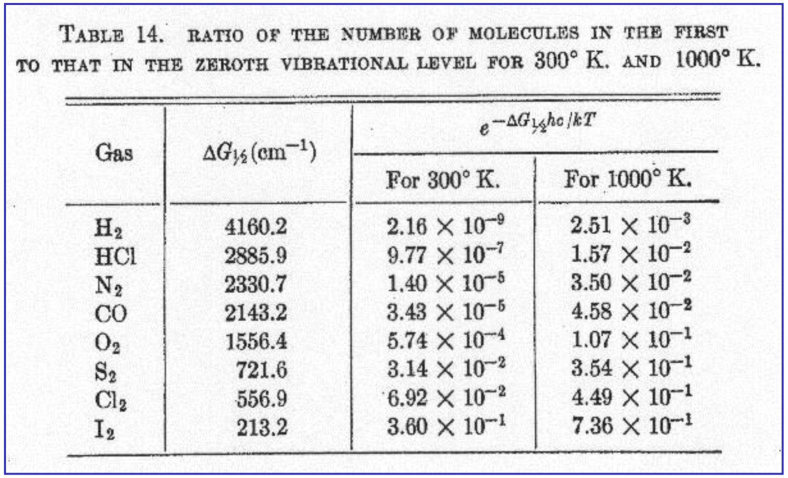


TABLE 14. RATIO OF THE NUMBER OF MOLECULES IN THE FIRST TO THAT IN THE ZEROTH VIBRATIONAL LEVEL FOR 300° K. AND 1000° K.

Gas	$\Delta G_{1/2}$ (cm^{-1})	$e^{-\Delta G_{1/2} hc/kT}$	
		For 300° K.	For 1000° K.
H_2	4160.2	2.16×10^{-9}	2.51×10^{-3}
HCl	2885.9	9.77×10^{-7}	1.57×10^{-2}
N_2	2330.7	1.40×10^{-5}	3.50×10^{-2}
CO	2143.2	3.43×10^{-5}	4.58×10^{-2}
O_2	1556.4	5.74×10^{-4}	1.07×10^{-1}
S_2	721.6	3.14×10^{-2}	3.54×10^{-1}
Cl_2	556.9	6.92×10^{-2}	4.49×10^{-1}
I_2	213.2	3.60×10^{-1}	7.36×10^{-1}

Note: not always thermodynamic equilibrium

Population distributions; rotational states in a diatomic molecule

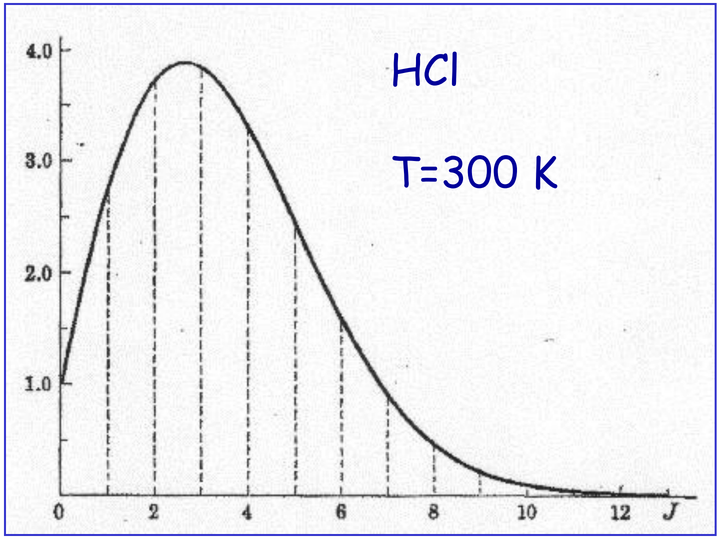
Probability of finding a molecule in a rotational quantum state:

$$P(J) = \frac{(2J+1)e^{-E_{rot}/kT}}{\sum_{J'}(2J'+1)e^{-E_{rot}/kT}}$$

$$= \frac{1}{Z_{rot}}(2J+1)e^{-BJ(J+1)+DJ^2(J+1)^2}$$

Find optimum via

$$\frac{dP(J)}{dJ} = 0$$



K_μ sensitivity coefficients to μ-variation for Lyman-α transition

Definition of sensitivity coefficient:

$$\frac{\Delta\nu}{\nu} = K_\mu \frac{\Delta\mu}{\mu}$$

Calculation for Lyman-α transition

$$\nu = \frac{E_2 - E_1}{h} = \frac{3}{4} R_\infty c \left(\frac{\mu_{red}}{m_e} \right)$$

with

$$\frac{\mu_{red}}{m_e} = \frac{1}{m_e} \left(\frac{M_p m_e}{M_p + m_e} \right) = \frac{M_p / m_e}{1 + M_p / m_e} = \frac{\mu}{1+\mu}$$

So (note energy scale drops out !):

$$\frac{\Delta\nu}{\nu} = \frac{\Delta(E_2 - E_1)}{E_2 - E_1} = \frac{\dfrac{\mu+\Delta\mu}{1+\mu+\Delta\mu} - \dfrac{\mu}{1+\mu}}{\mu/(1+\mu)} = \frac{\Delta\mu/\mu}{1+\mu+\Delta\mu} = K_\mu \frac{\Delta\mu}{\mu}$$

$$\longrightarrow \quad K_\mu = \frac{1}{1+\mu+\Delta\mu} \sim 5.4 \times 10^{-4}$$

Isotope effects in molecules + sensitivity for μ-variation

Electronic

Born-Oppenheimer: the derivative of electronic wave function w.r.t nuclear coordinates is small:

$$\longrightarrow \qquad \nabla_A \psi_{\text{el}} \approx 0$$

Electronic wave functions and energies do not depend on nuclear masses (compare the case of the atom)

Mass dependences

In the above mass dependences expressed as "reduced mass";
Note that we assume:

$$\mu \propto \mu_{red}$$

Proportionality with "baryonic mass" (neutrons and protons)

Isotope effects in molecules + sensitivity for μ-variation

Vibrational energy: $E_{\mathrm{vib}} = \hbar\sqrt{\frac{k}{\mu}}\left(v + \frac{1}{2}\right)$

K-coefficient for purely vibrational transition (overtone included):

$$\frac{\Delta\nu}{\nu} = \frac{\Delta(E_n - E_m)}{E_n - E_m} = \frac{\frac{1}{\sqrt{\mu+\Delta\mu}}\left[(n+1/2)-(m+1/2)\right] - \frac{1}{\sqrt{\mu}}\left[(n+1/2)-(m+1/2)\right]}{1/\sqrt{\mu}\left[(n+1/2)-(m+1/2)\right]} = \frac{\sqrt{\mu}}{\sqrt{\mu+\Delta\mu}} - 1$$

$$\approx 1 - \frac{1}{2}\frac{\Delta\mu}{\mu} - 1 = K_\mu \frac{\Delta\mu}{\mu}$$

So: $K_\mu = -\frac{1}{2}$ For ALL vibrational transitions

Isotope effects in molecules + sensitivity for μ-variation

Rotational energy:

$$E_{\mathrm{rot}} = \hbar^2 \frac{N(N+1)}{2\mu R_e^2} \qquad \nu = \frac{\hbar}{2\mu R_e^2}\left[N_2(N_2+1) - N_1(N_1+1)\right] = \frac{C}{\mu}$$

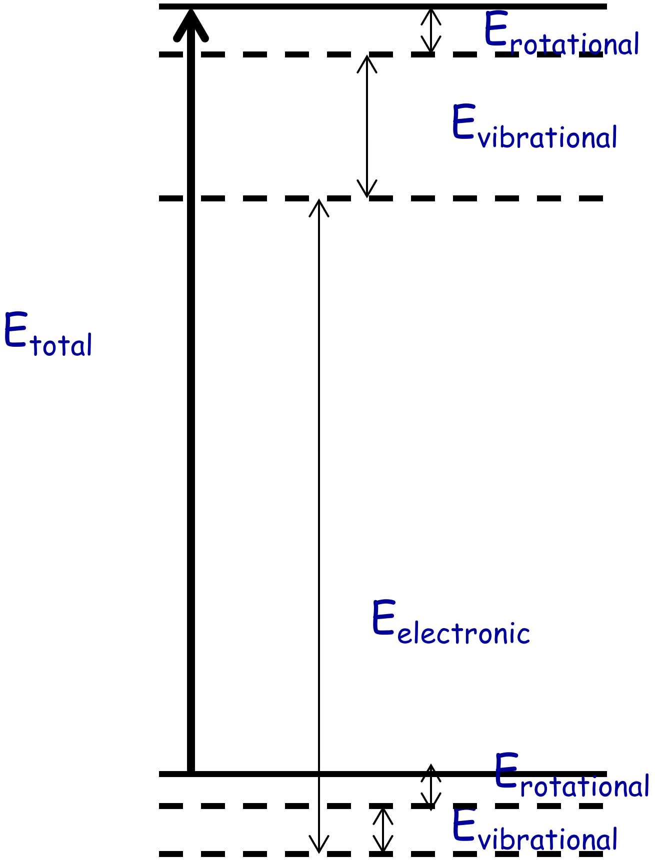
K-coefficient for purely rotational transition :

$$\frac{\Delta\nu}{\nu} = K_\mu \frac{\Delta\mu}{\mu} \longrightarrow \qquad K_\mu = \frac{\mu}{\nu}\frac{\Delta\nu}{\Delta\mu} = \frac{\mu}{\nu}\frac{d\nu}{d\mu} = \mu\frac{\mu}{C}\left(-C\mu^{-2}\right) = -1$$

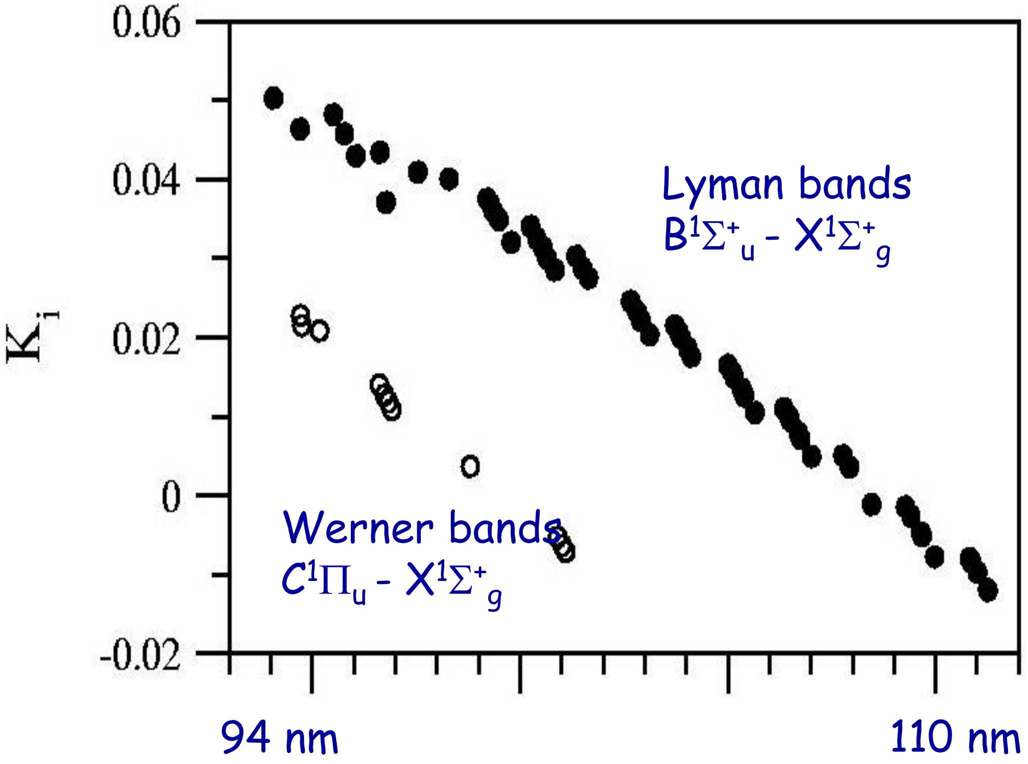
So:

$$\boxed{K_\mu = -1}$$

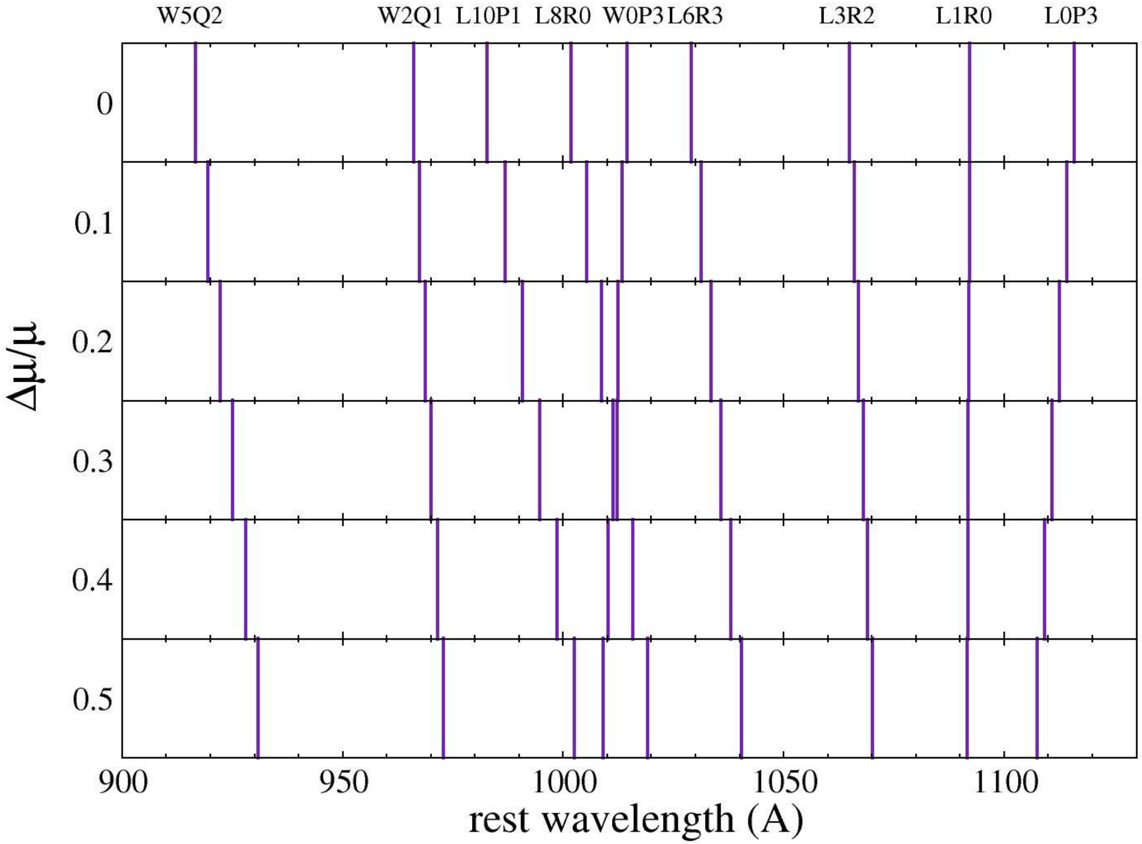
Isotope effects in molecules + sensitivity for μ-variation



For H_2



K_i different for H_2 lines



red shifter

anchor

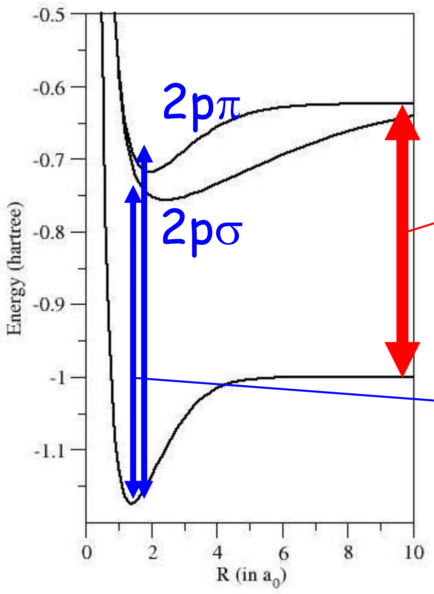
blue shifter

Electronic spectra of H_2

Composition of the universe:

80 % hydrogen H/H_2
20 % helium
<0.1% other elements

H_2

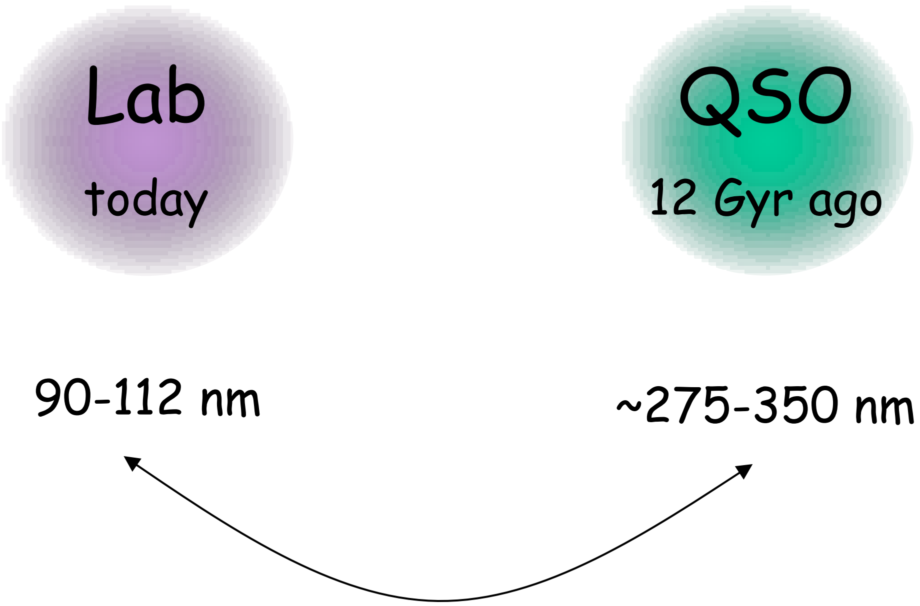


H (Lyman-α) ~ 121 nm

H_2, Lyman en Werner BANDS
~90 - 110 nm
Extreme Ultraviolet Wavelengths

Empirical search for a change in μ

- Spectroscopy
- Compare H_2 spectra in different epochs:



Lab

today

QSO

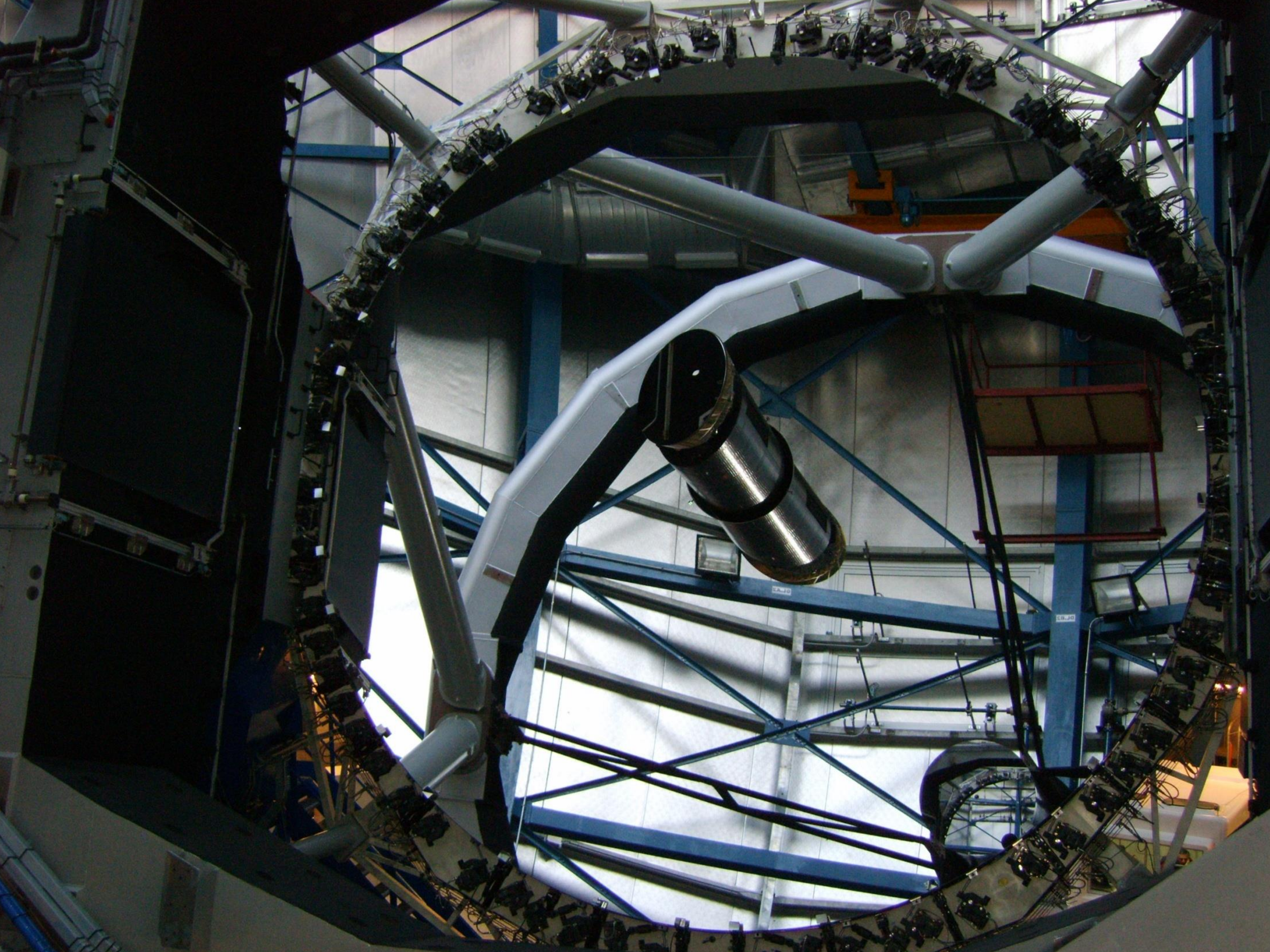
12 Gyr ago

90-112 nm

~275-350 nm

$$\frac{\lambda_i}{\lambda_i^0} \equiv 1 + z_i$$ Cosmological reshift

Atmospheric transmission
only for z>2

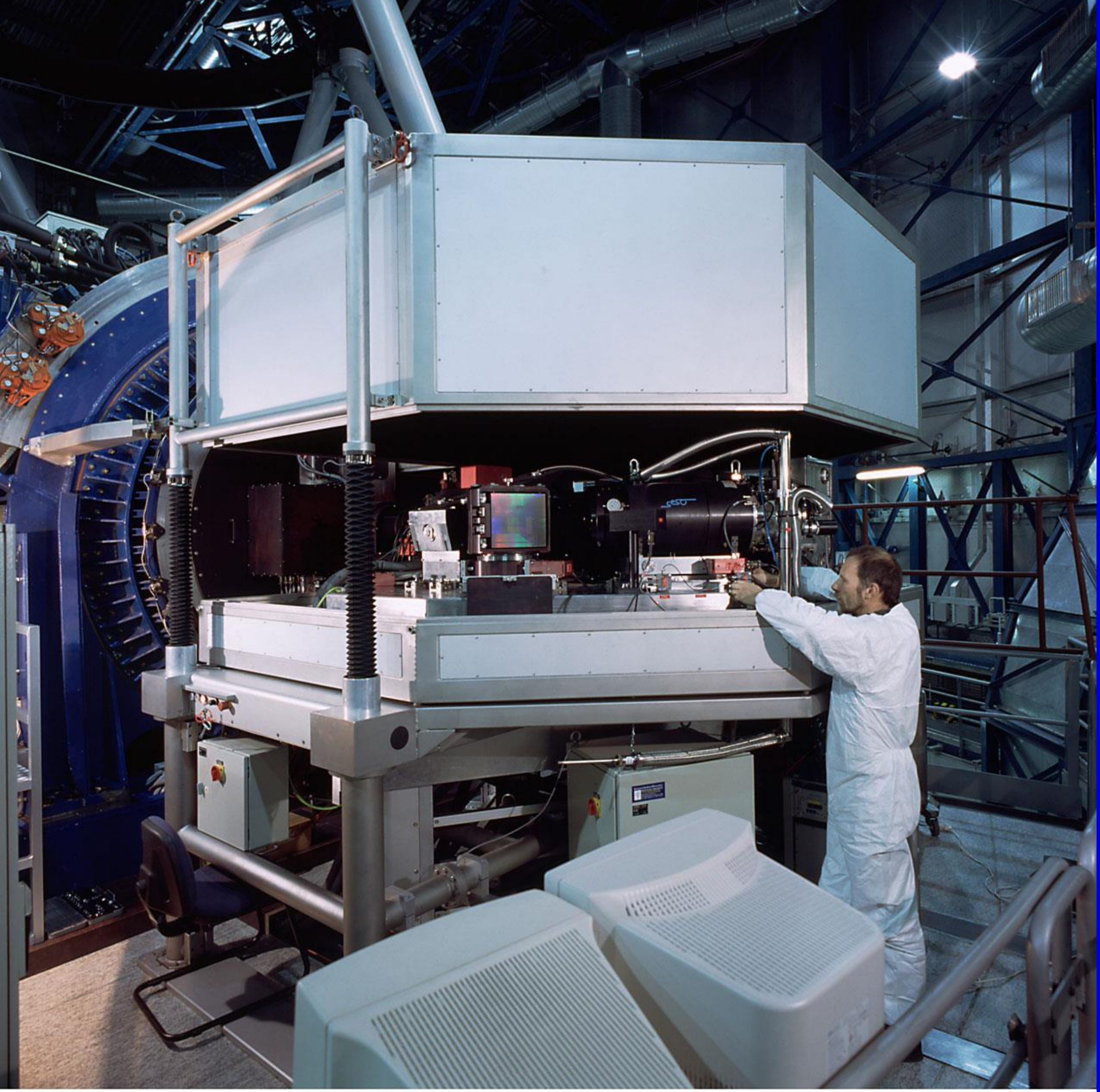


Q2348-011
z = 2.42

Magnitude
18.4

ESO-VLT
2007

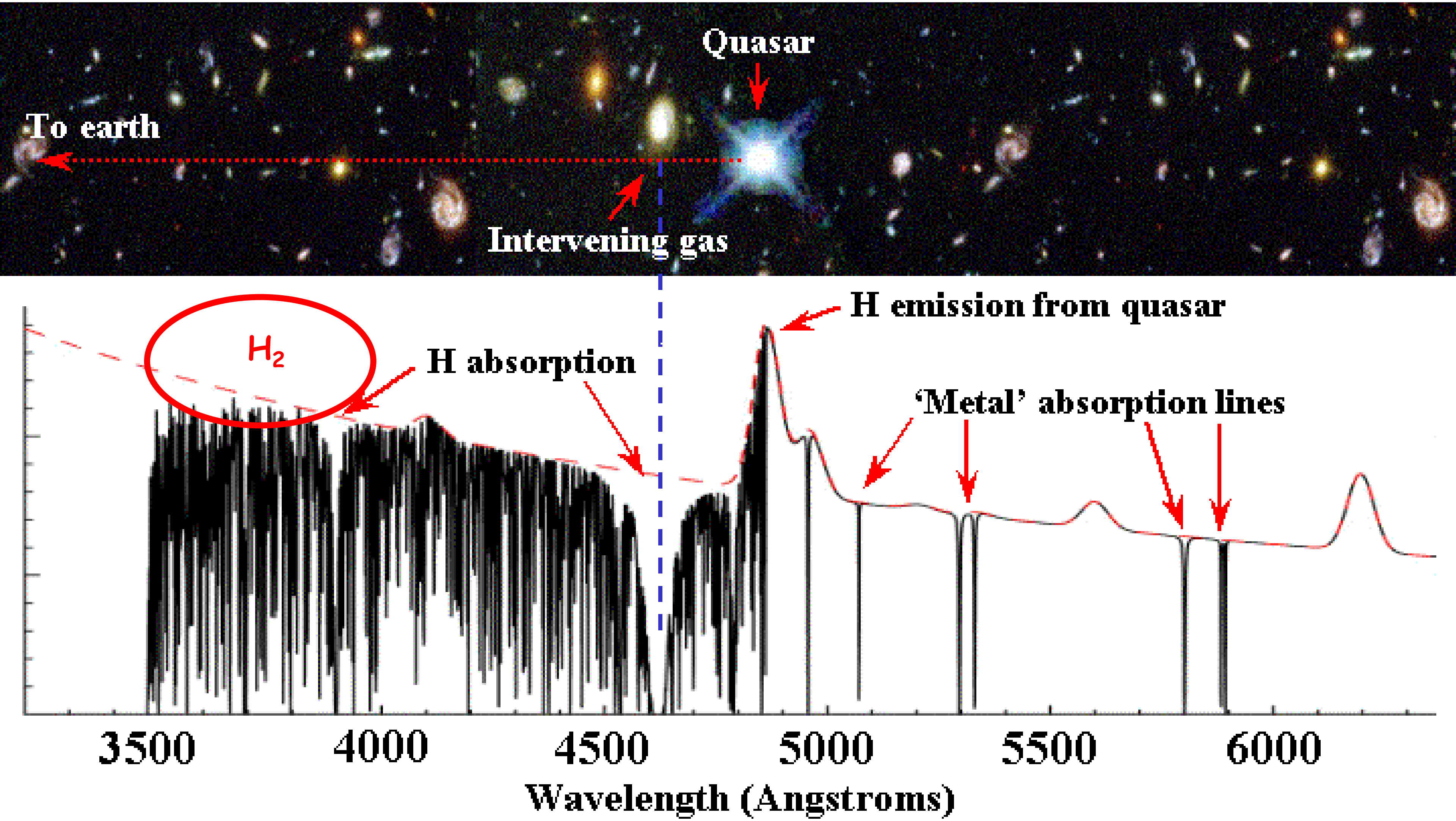
UVES:
Ultraviolet – Visual Echelle Spectrograph



UVES at Kueyen

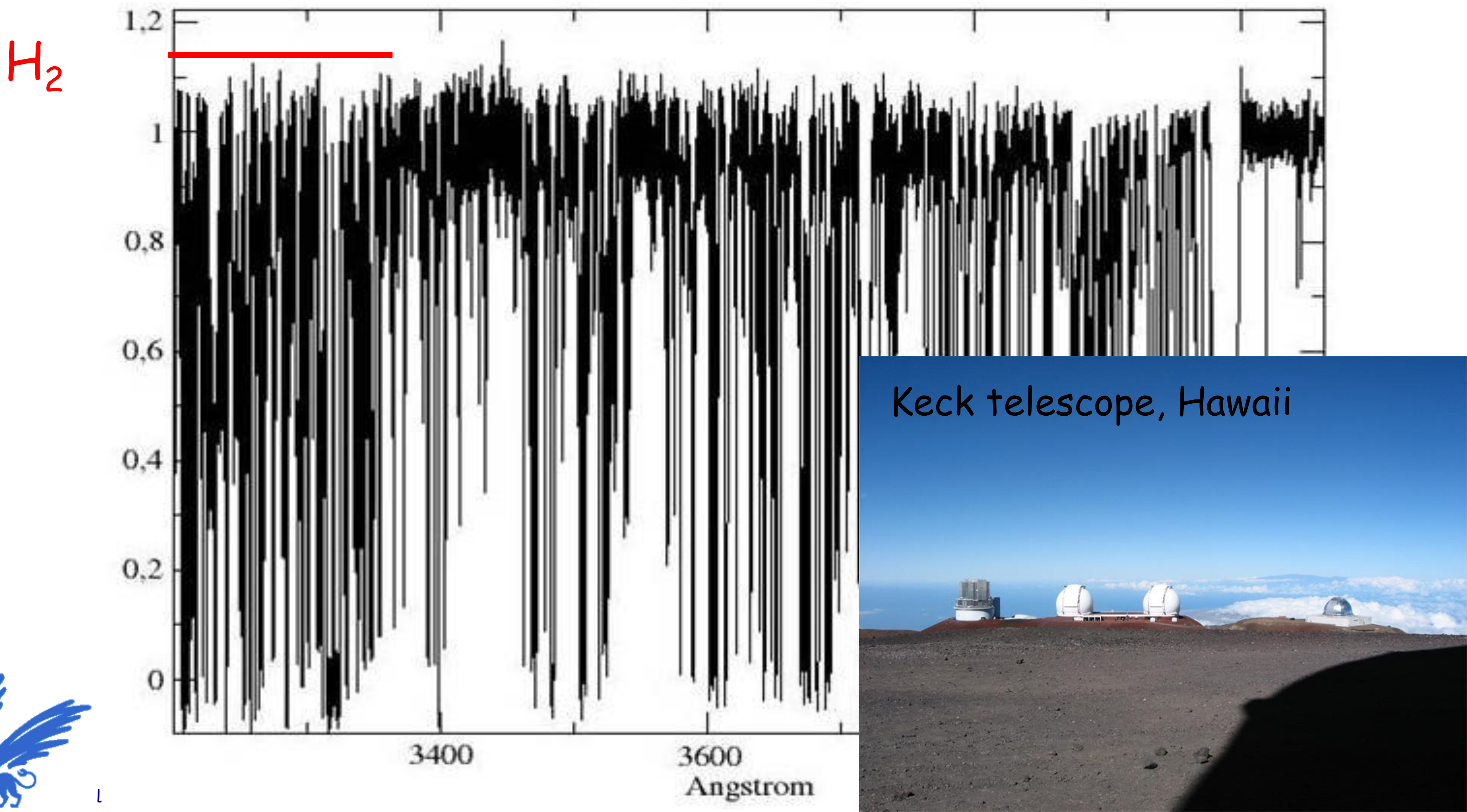
ESO PR Photo 43e/99 (8 December 1999)

Empirical search for a change in μ: quasars



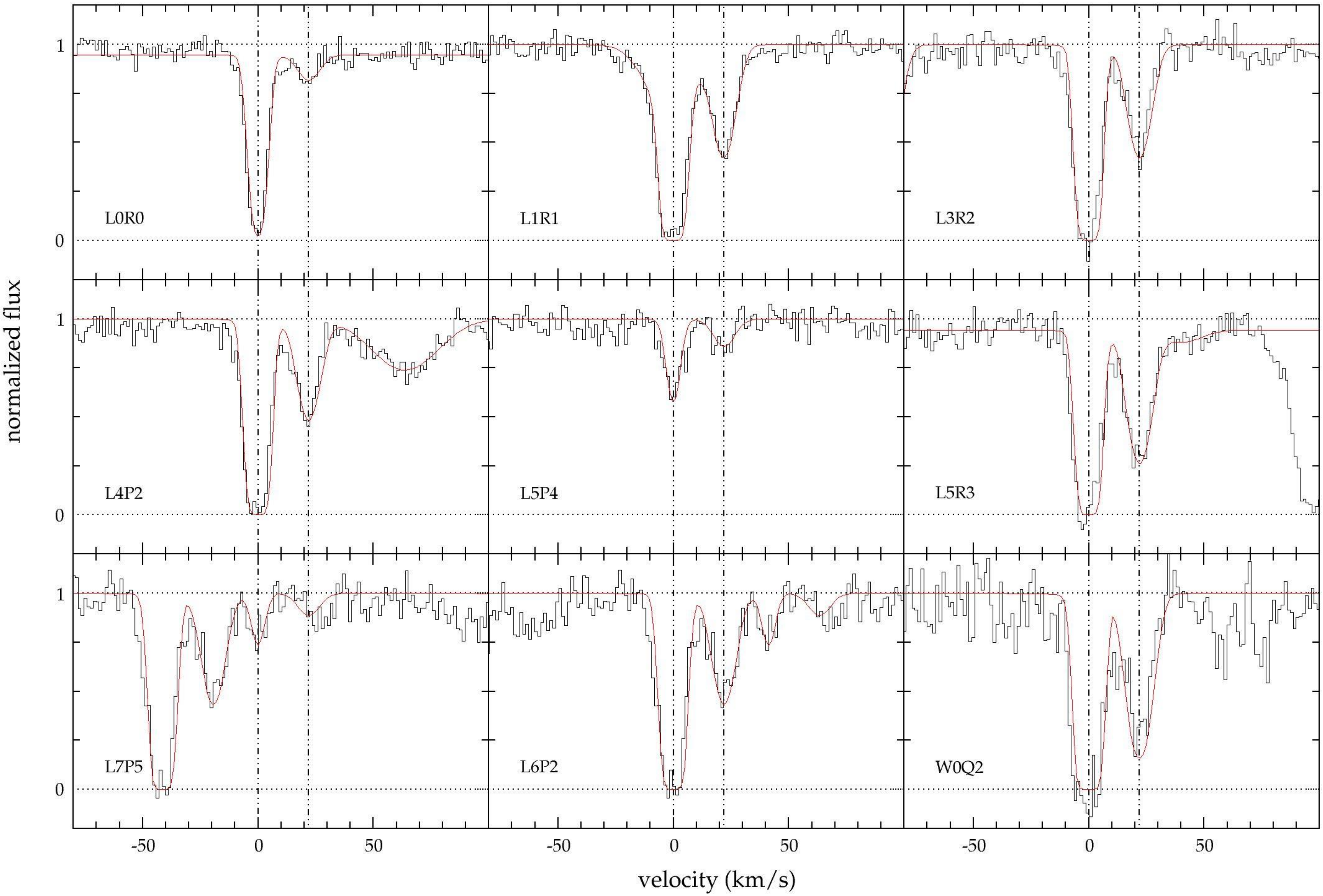
J2123 from HIRES-Keck at Hawaii (normalized)

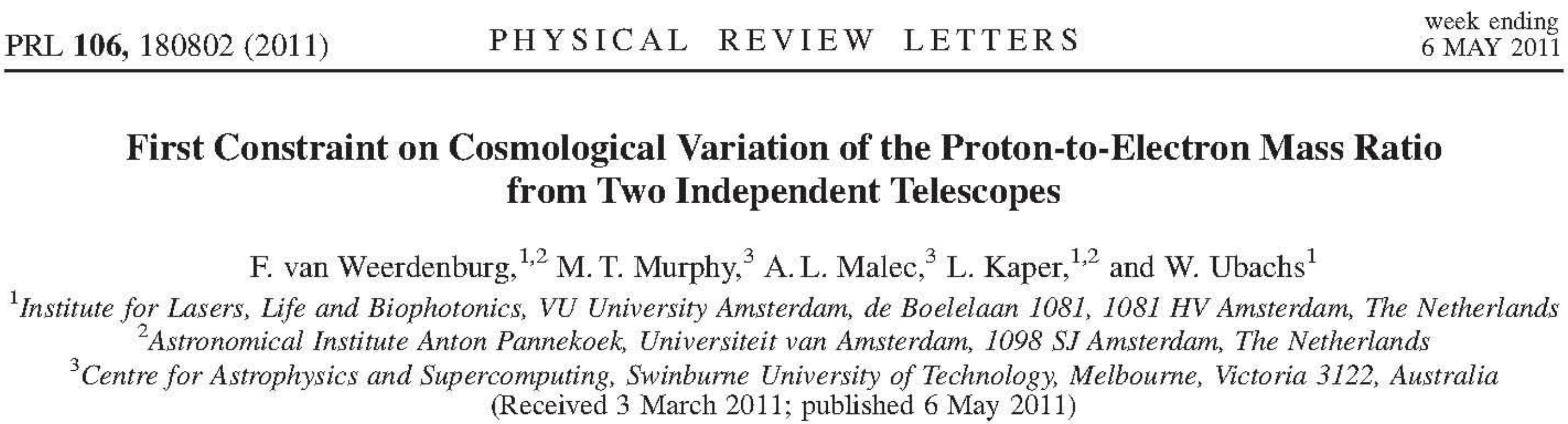
Resolution 110000 ; z_{abs}=2.0593



Keck telescope, Hawaii

J2123, $z_{abs} = 2.0593426$, H2 lines





PRL **106,** 180802 (2011) PHYSICAL REVIEW LETTERS week ending 6 MAY 2011

First Constraint on Cosmological Variation of the Proton-to-Electron Mass Ratio from Two Independent Telescopes

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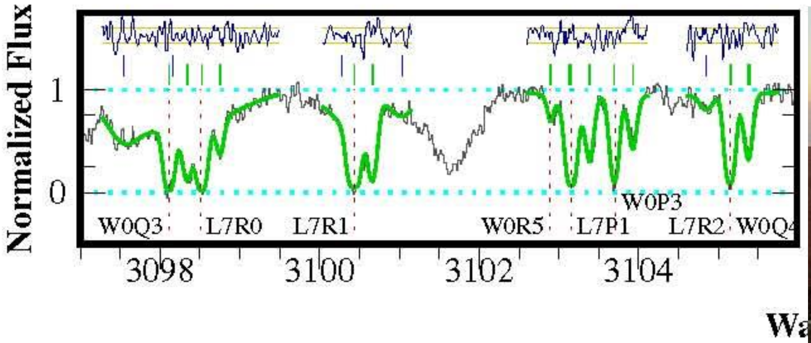


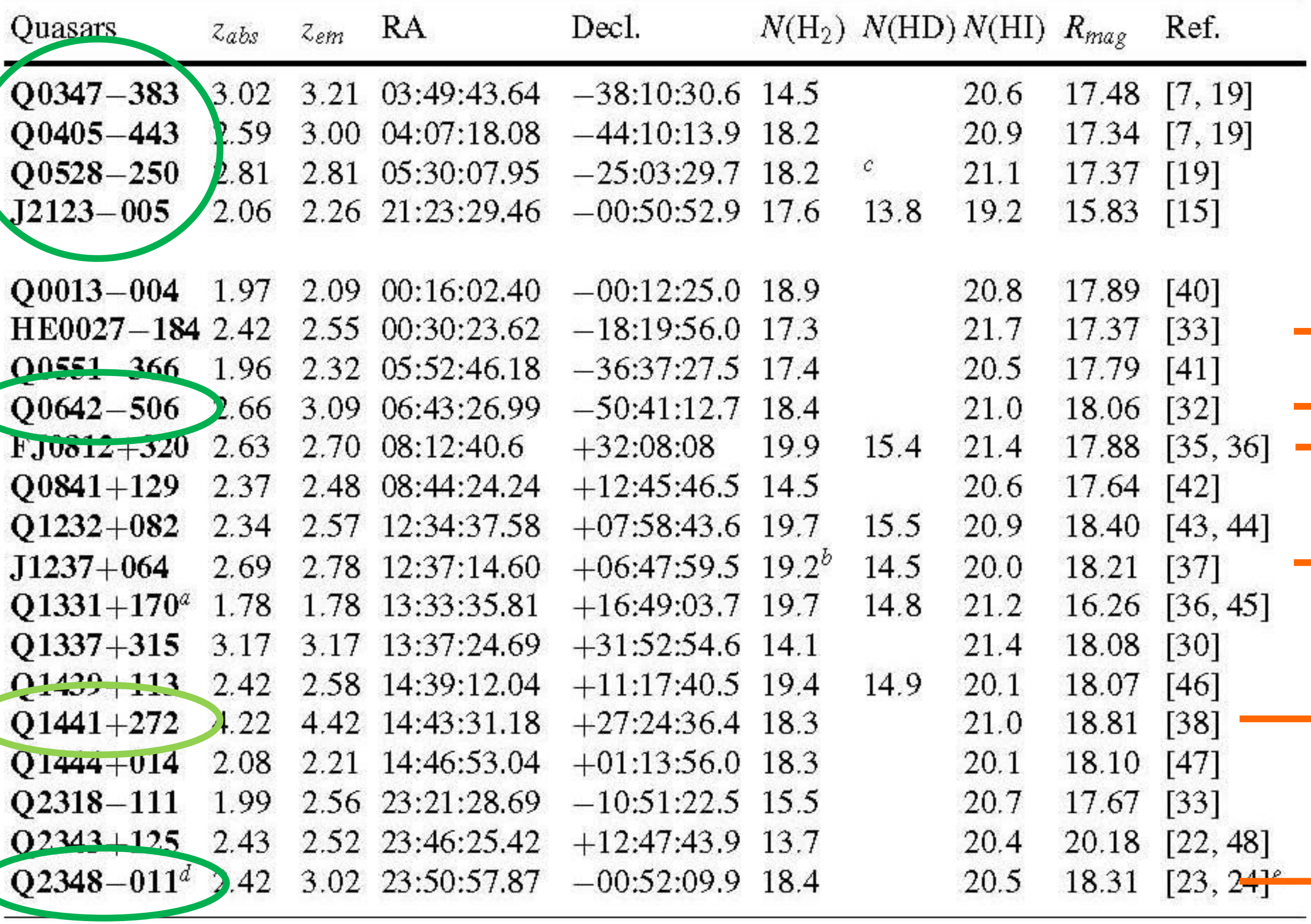
Keck:

$\Delta\mu/\mu = (5.6 \pm 5.5_{stat} \pm 2.9_{syst}) \times 10^{-6}$

VLT:

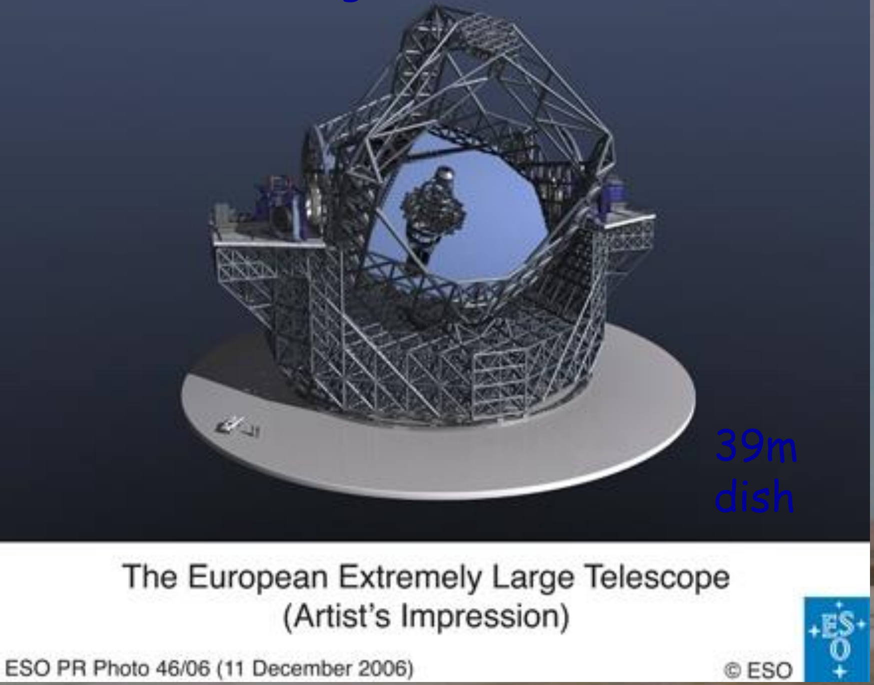
$\Delta\mu/\mu = (8.5 \pm 3.6_{stat} \pm 2.2_{syst}) \times 10^{-6}$

How much H2 at high redshift?



Quasars	z_{abs}	z_{em}	RA	Decl.	$N(H_2)$	$N(HD)$	$N(HI)$	R_{mag}	Ref.	
Q0347−383	3.02	3.21	03:49:43.64	−38:10:30.6	14.5		20.6	17.48	[7, 19]	Done
Q0405−443	2.59	3.00	04:07:18.08	−44:10:13.9	18.2		20.9	17.34	[7, 19]	Done
Q0528−250	2.81	2.81	05:30:07.95	−25:03:29.7	18.2	^{c}	21.1	17.37	[19]	Done
J2123−005	2.06	2.26	21:23:29.46	−00:50:52.9	17.6	13.8	19.2	15.83	[15]	Done
Q0013−004	1.97	2.09	00:16:02.40	−00:12:25.0	18.9		20.8	17.89	[40]	
HE0027−184	2.42	2.55	00:30:23.62	−18:19:56.0	17.3		21.7	17.37	[33]	→ Analysis
Q0551−366	1.96	2.32	05:52:46.18	−36:37:27.5	17.4		20.5	17.79	[41]	
Q0642−506	2.66	3.09	06:43:26.99	−50:41:12.7	18.4		21.0	18.06	[32]	→ Analysis
FJ0812+320	2.63	2.70	08:12:40.6	+32:08:08	19.9	15.4	21.4	17.88	[35, 36]	→ ?
Q0841+129	2.37	2.48	08:44:24.24	+12:45:46.5	14.5		20.6	17.64	[42]	
Q1232+082	2.34	2.57	12:34:37.58	+07:58:43.6	19.7	15.5	20.9	18.40	[43, 44]	
J1237+064	2.69	2.78	12:37:14.60	+06:47:59.5	19.2^b	14.5	20.0	18.21	[37]	→ ? (+ CO)
Q1331+170^a	1.78	1.78	13:33:35.81	+16:49:03.7	19.7	14.8	21.2	16.26	[36, 45]	
Q1337+315	3.17	3.17	13:37:24.69	+31:52:54.6	14.1		21.4	18.08	[30]	
Q1439+113	2.42	2.58	14:39:12.04	+11:17:40.5	19.4	14.9	20.1	18.07	[46]	
Q1441+272	4.22	4.42	14:43:31.18	+27:24:36.4	18.3		21.0	18.81	[38]	→ VLT 2013
Q1444+014	2.08	2.21	14:46:53.04	+01:13:56.0	18.3		20.1	18.10	[47]	
Q2318−111	1.99	2.56	23:21:28.69	−10:51:22.5	15.5		20.7	17.67	[33]	
Q2343+125	2.43	2.52	23:46:25.42	+12:47:43.9	13.7		20.4	20.18	[22, 48]	
Q2348−011^d	2.42	3.02	23:50:57.87	−00:52:09.9	18.4		20.5	18.31	[23, 24]^e	→ Done 2012

The rise of a giant



39m dish

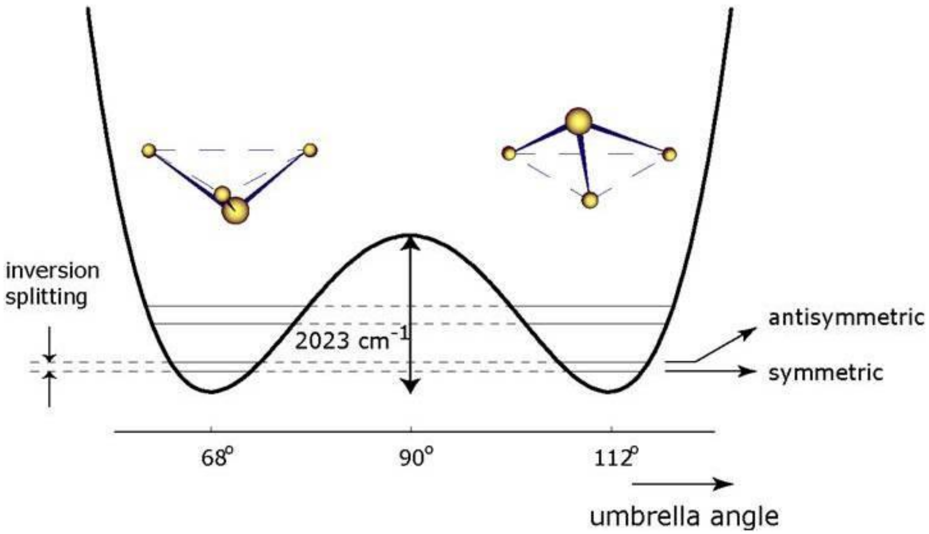
The European Extremely Large Telescope
(Artist's Impression)

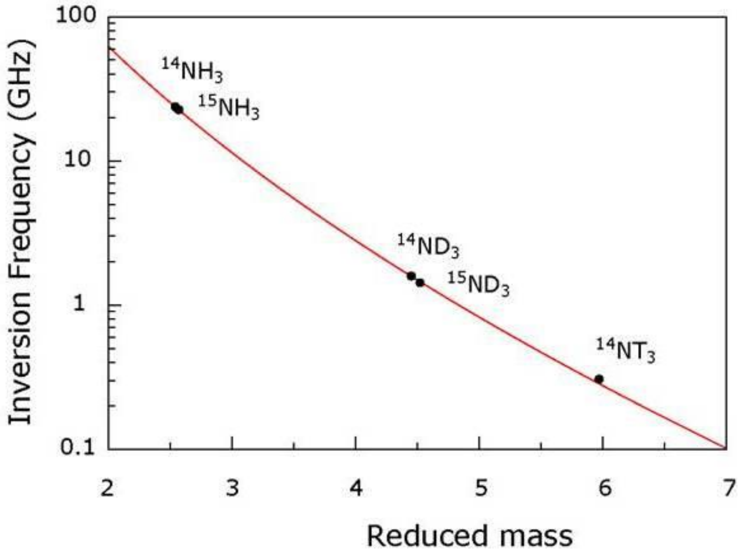
ESO PR Photo 46/06 (11 December 2006)

© ESO

Outlook: More sensitive molecules

Quantum tunneling





$K = -4.2$

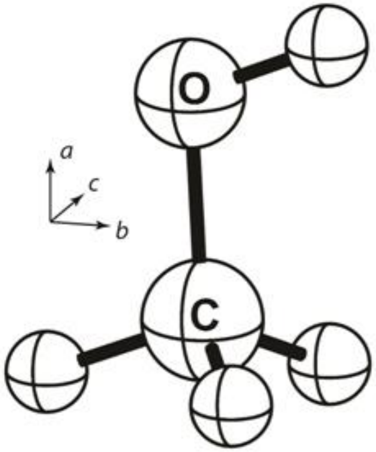
Outlook: More sensitive molecules

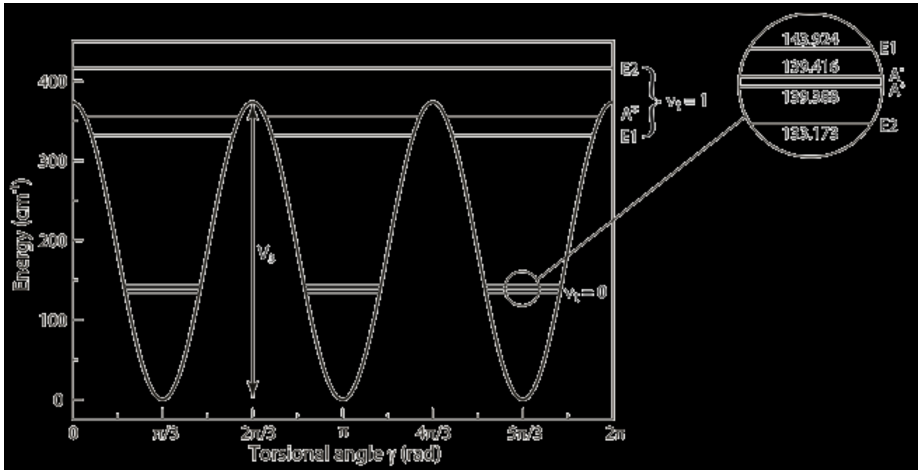
Quantum tunneling

PRL **106,** 100801 (2011) PHYSICAL REVIEW LETTERS week ending 11 MARCH 2011

Methanol as a Sensitive Probe for Spatial and Temporal Variations of the Proton-to-Electron Mass Ratio

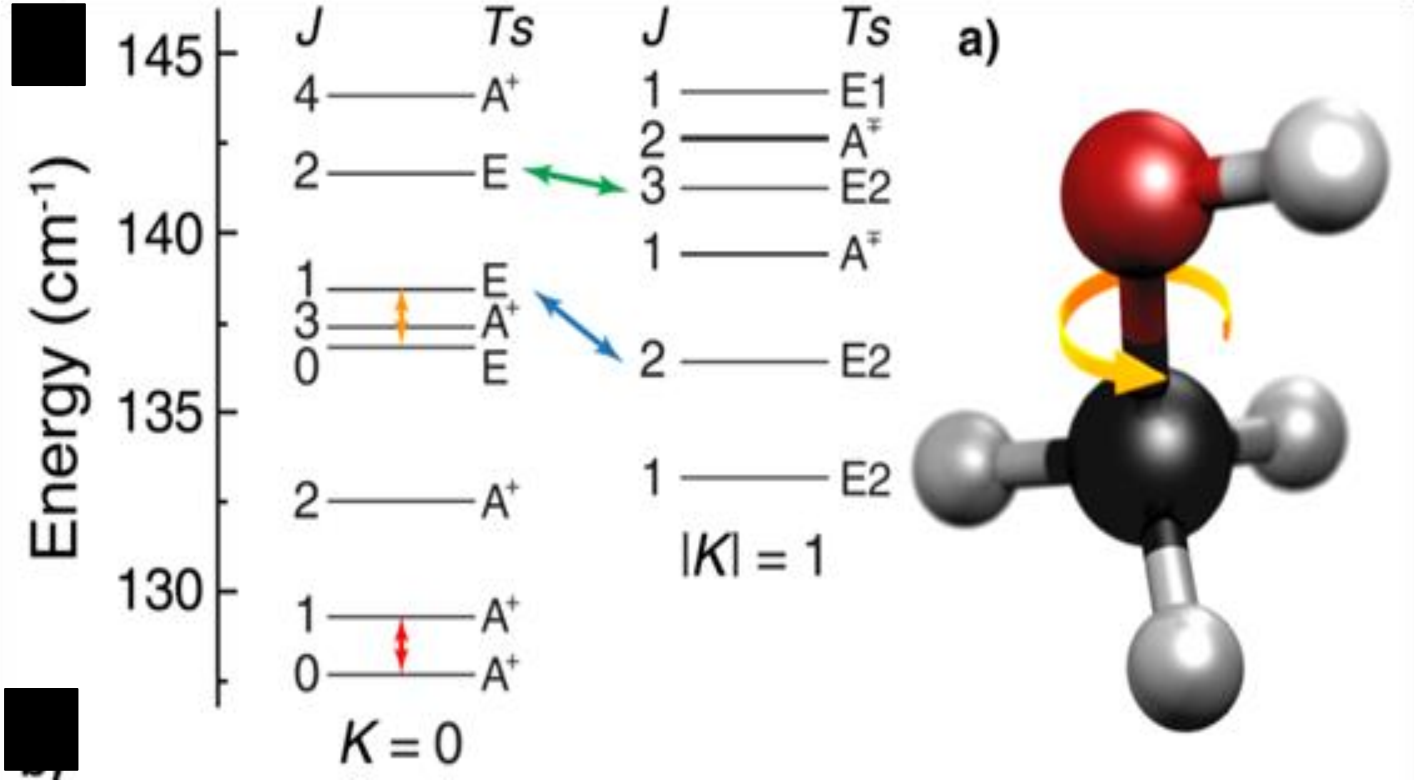
Paul Jansen,[1] Li-Hong Xu,[2] Isabelle Kleiner,[3] Wim Ubachs,[1] and Hendrick L. Bethlem[1]





Calculations ⟶ Extreme shifters

Extreme shifters; towards radio astronomy


[redacted]

[redacted]

48372.4558 MHz; K=-1

48376.892 MHz; K=-1

12178.597 MHz; K=-33

60531.1489 MHz; K=-7

Effelsberg Radio Telescope

Effelsberg Radio Telescope

PKS-1830-211

at z=0.88582
(7 Gyrs look-back)