Lectures ICTP Winter School on Optics 2016

Precision Spectroscopy of Molecular Hydrogen

and Physics Beyond the Standard Model

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Topics:

1) Level structure and spectroscopy of the hydrogen molecule
2) Probe for a varying proton-electron mass ratio from H_2
3) New forces and dimensions from precision studies of H_2

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Reading Material:

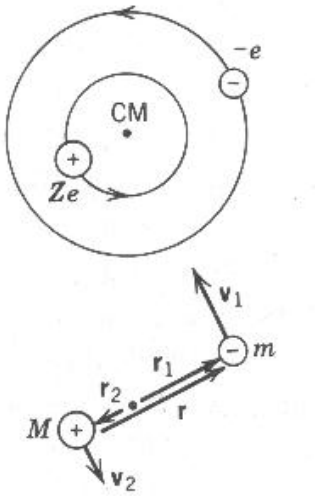
Physics beyond the Standard Model from hydrogen spectroscopy

W. Ubachs et al., J. Mol. Spectr. 320 (2016) 1-12

Search for a drifting proton-electron mass ratio from H_2

W. Ubachs et al., Rev. Mod. Phys. April (2016); ArXiv:1511.04476

The Hydrogen Atom



Reduced mass: transformation from two → one particle problem

$$\mu_{red} = \frac{mM}{m+M} \qquad \mu = \frac{M}{m}$$

$$E_n = -\frac{1}{n^2}\frac{\mu_{red}}{m_e}R_\infty$$

Rydberg constant

$$R_\infty = \left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 \frac{m_e}{2\hbar^2}$$

Niels Bohr

The Proton-Electron Mass Ratio

From experiments:
Fundamental Dimensionless Constant of Nature

$$\mu = \frac{M_p}{m_e} = 1836.15267245(75)$$

The Ratio of Proton and Electron Masses

FRIEDRICH LENZ
Düsseldorf, Germany
(Received April 5, 1951)

THE most exact value at present[1] for the ratio of proton to electron mass is 1836.12 ± 0.05. It may be of interest to note that this number coincides with $6\pi^5 = 1836.12$.

[1] Sommer, Thomas, and Hipple, Phys. Rev. **80**, 487 (1950).

Physical Review 82 (1951) 554

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-a transition

$$\nu = \frac{E_2 - E_1}{h} = \frac{3}{4} R_\infty c \left(\frac{\mu_{red}}{m_e} \right) \qquad \text{with} \qquad \frac{\mu_{red}}{m_e} = \frac{1}{m_e}\left(\frac{M_p m_e}{M_p + m_e} \right) = \frac{M_p / m_e}{1 + M_p / m_e} = \frac{\mu}{1+\mu}$$

So (note energy scale drops out !):

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

$$\longrightarrow \quad K_\mu = \frac{1}{1+\mu+\Delta\mu} \sim 5.4\times10^{-4}$$

Atoms are insensitive !

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:

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

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

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

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

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

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

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

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

Nuclei can be considered stationary. Then:

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

Separation of variables is possible.

Insert results in the Schrödinger equation:

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

Separation of variables in the molecular Hamiltonian

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

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

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

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

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

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

Schrodinger equation for the nuclear motion

The previous analysis yields:

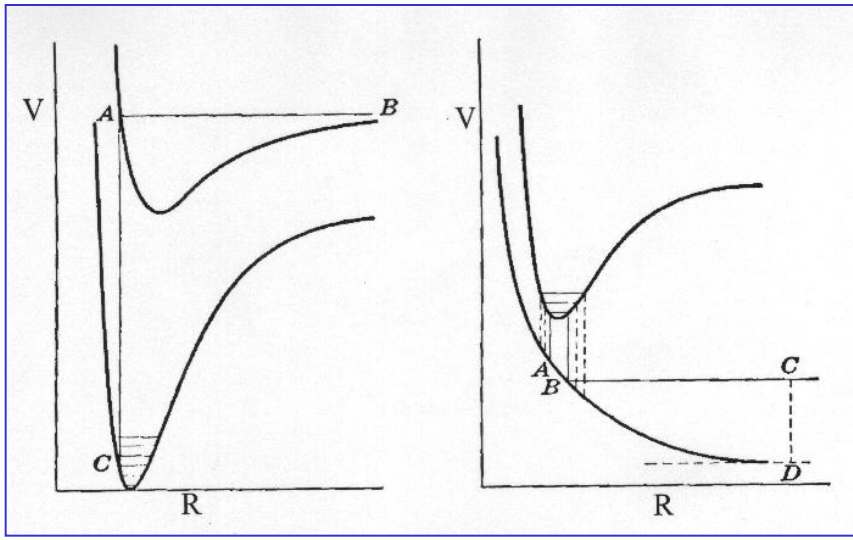
$$\left\{-\sum_A \frac{\hbar^2}{2M_A}\nabla_A^2 + \sum_{A>B}\frac{Z_A Z_B e^2}{4\pi\varepsilon_0|R_A - R_B|} + E_{el}(\vec{R})\right\}\chi_{\text{nuc}} = E_{\text{total}}\chi_{\text{nuc}}$$

This is a Schrödinger equation with a potential energy:

$$V(\vec{R}) = \sum_{A>B}\frac{Z_A Z_B e^2}{4\pi\varepsilon_0|R_A - R_B|} + E_{\text{el}}(\vec{R})$$

nuclear repulsion chemical binding

Typical potential energy curves in molecules



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

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

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

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

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

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

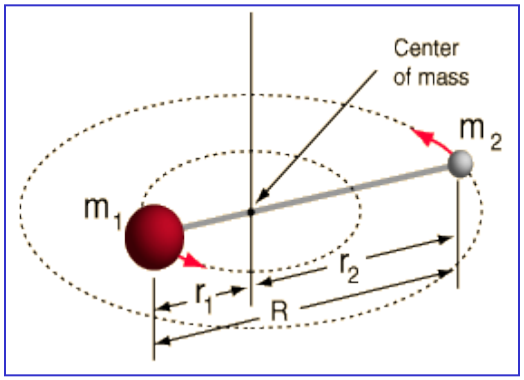
Hence the wave function of the molecule:

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

Reduction of molecular Schrödinger equation

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

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:

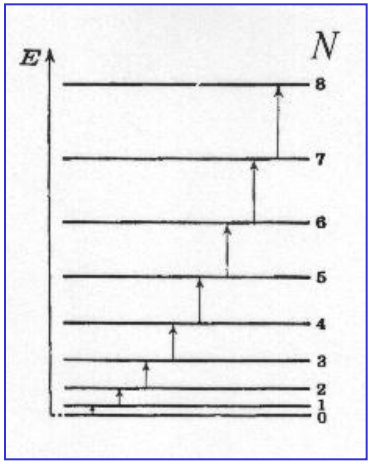
$$\left[-\frac{\hbar^2}{2\mu R^2} \frac{\partial}{\partial R}\left(R^2 \frac{\partial}{\partial R} \right) + \frac{1}{2\mu R^2} \vec{N}^2 + V(R) \right] \chi_{\text{nuc}}(R) = E_{\text{vib,rot}} \chi_{\text{nuc}}(R)$$

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

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

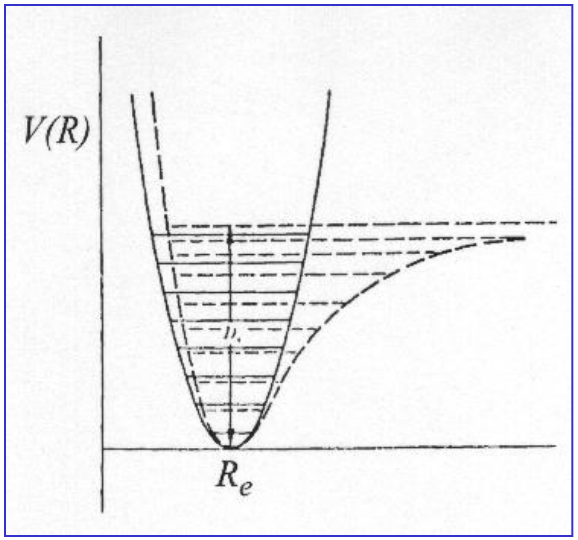
Vibrational motion

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

Non-rotation: $N=0$

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

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



Make a Taylor series expansion around $r=R-R_e$

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

$V(R_e)=0$ by choice

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

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

Vibrational motion - 2

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

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

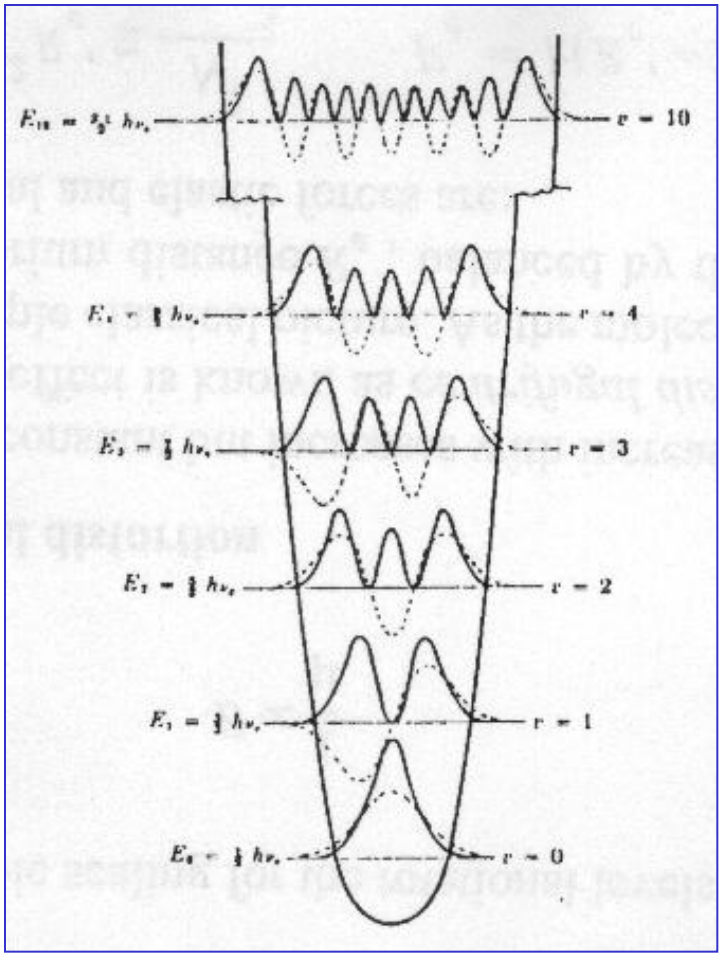
$$Q_v(\rho)=\frac{2^{v/2}\alpha^{1/4}}{\sqrt{v!}\pi^{1/4}}\exp\left[\frac{1}{2}\alpha\rho^2\right]H_v\left(\sqrt{\alpha}\rho\right)$$

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

Energy eigenvalues:

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

isotope effect



Finer details of the rovibrational motion

Centrifugal distortion:

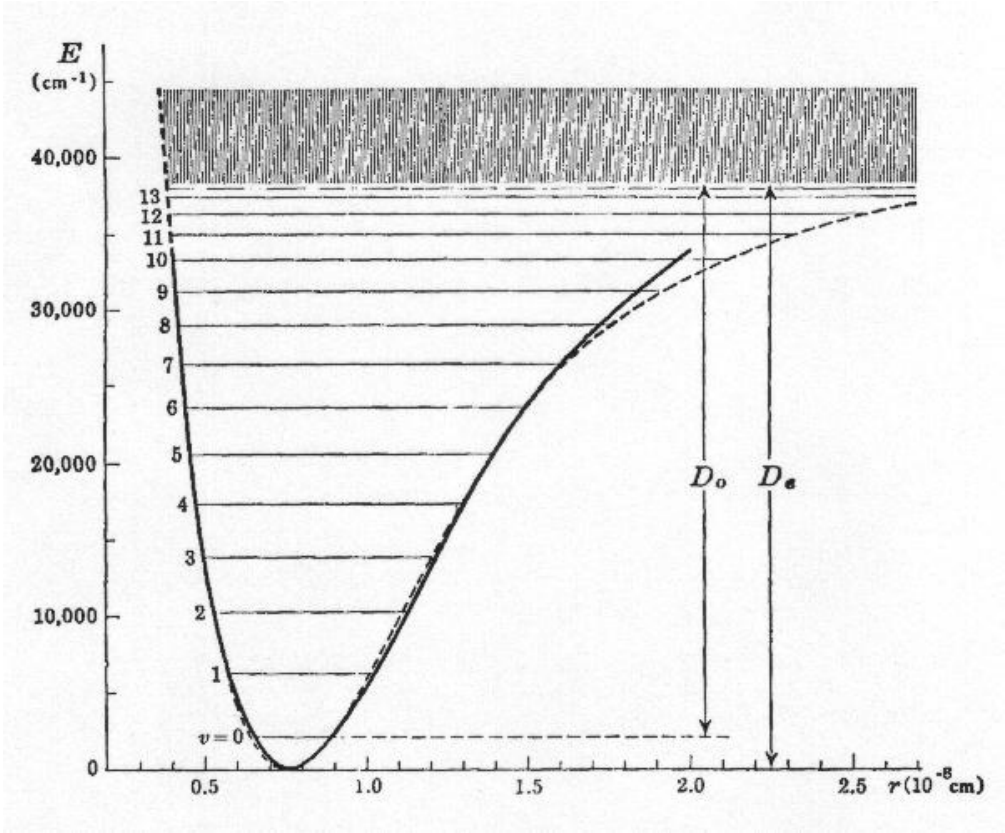
$$E_{\text{rot}} = BN(N+1) - DN^2(N+1)^2$$

Anharmonic vibrational motion

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

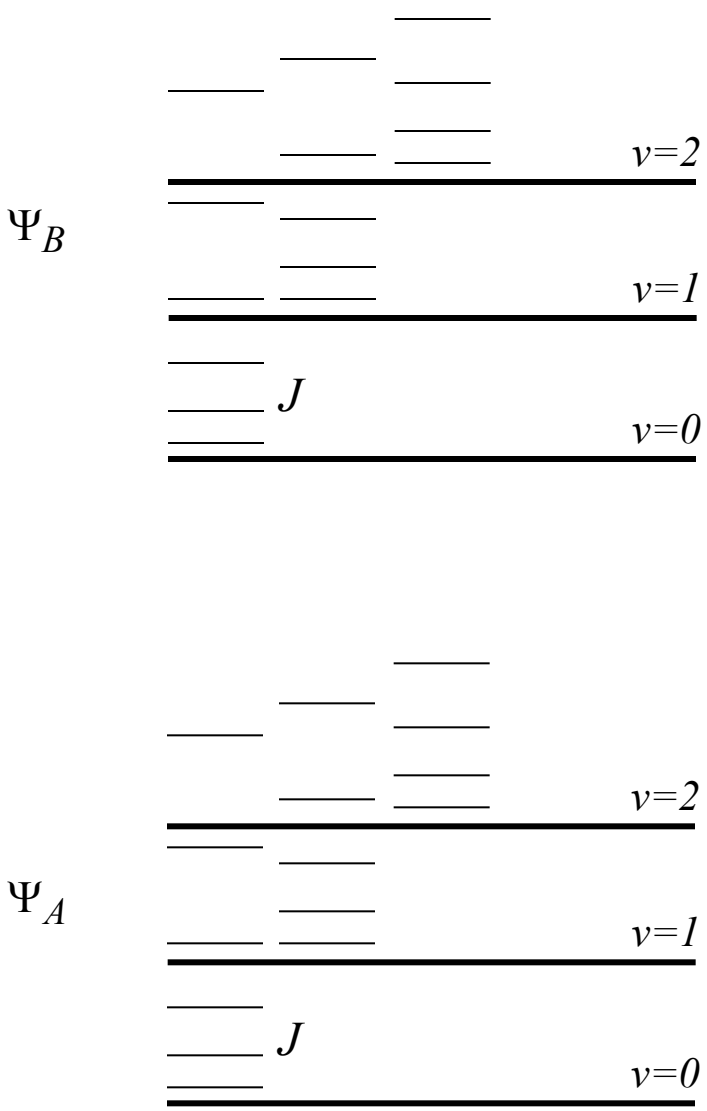
Dunham expansion:

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



Vibrational energies in the H_2-molecule

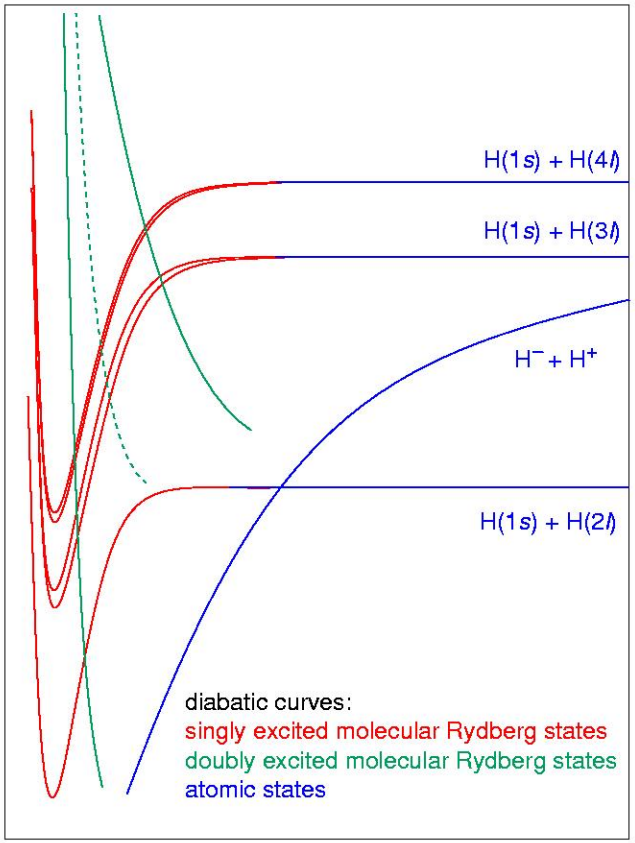
Energy levels in a molecule: general structure



Rovibrational structure superimposed on electronic structure

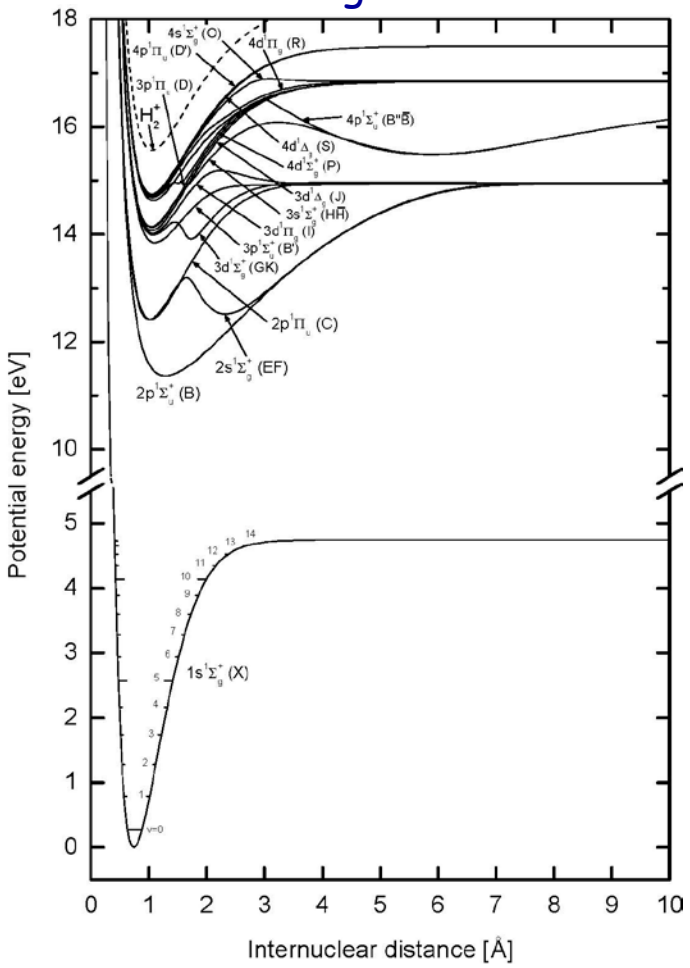
Electronic structure of the Hydrogen molecule

Diabatic Potentials

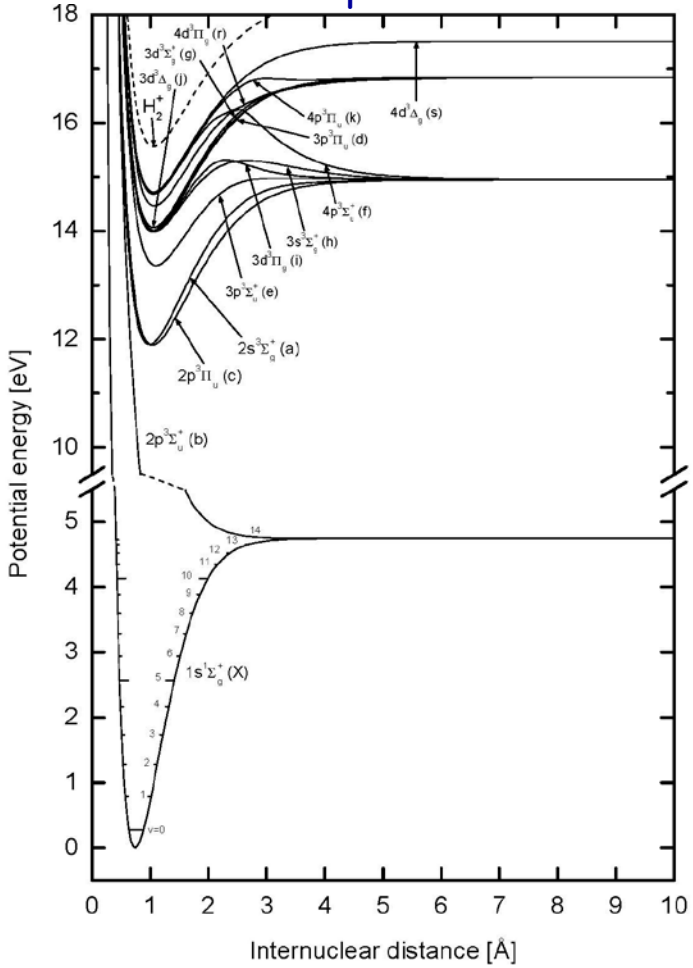


Singlet-Triplet structure in the Hydrogen molecule

singlets



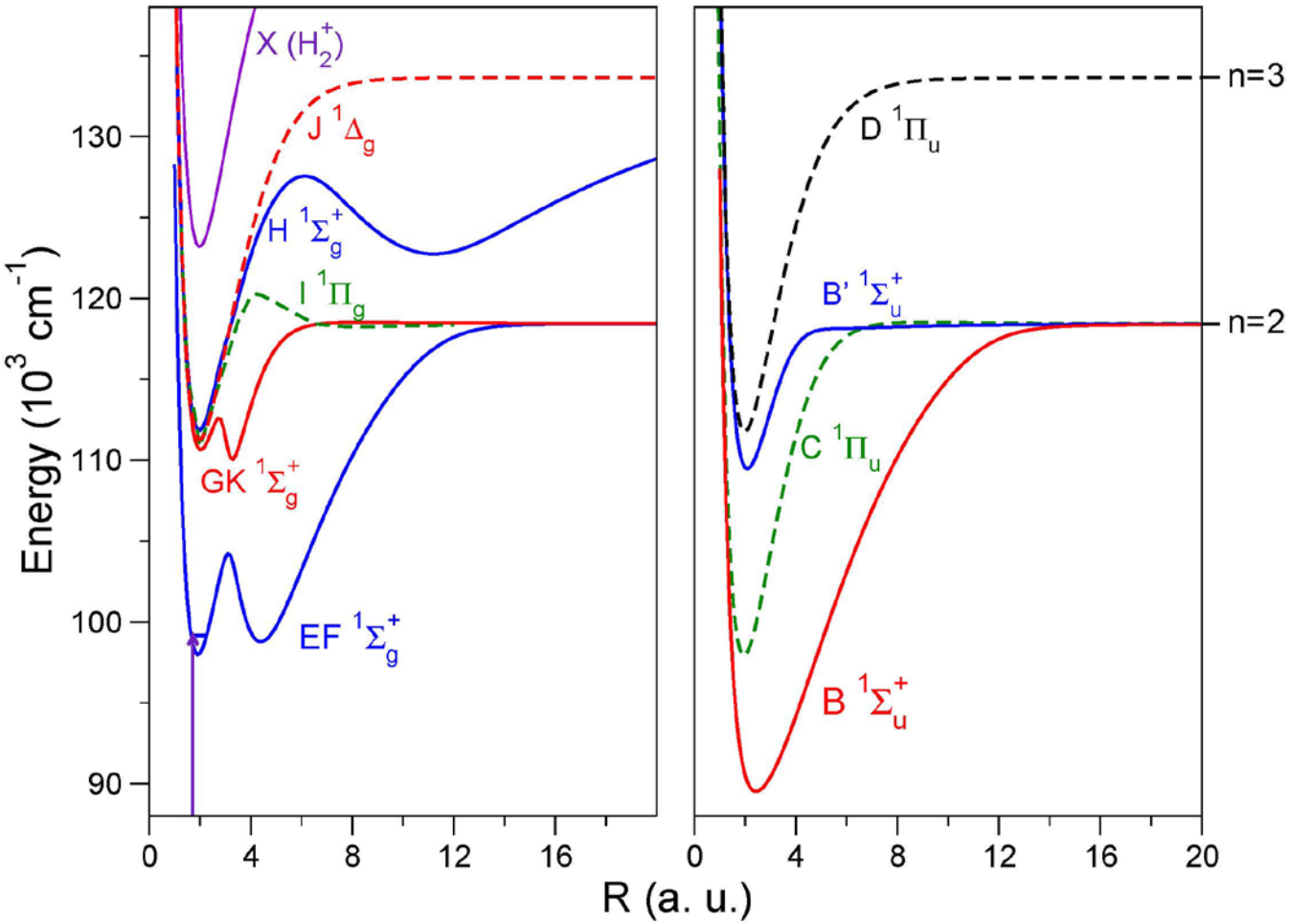
triplets



Very small $\vec{l} \cdot \vec{s}$ coupling

Electronic structure of the Hydrogen molecule; adiabatic

"gerade" "ungerade" Inversion symmetry



$X^1\Sigma_g^+$

is way below like H/He

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

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

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

Dipole transition between two states

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

Two different types of transitions

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

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

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

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:

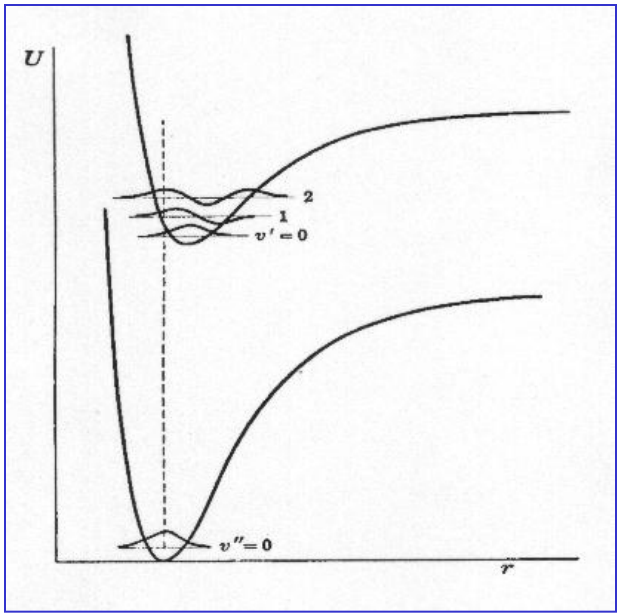
$$\overline{M}_e(R) = \int \psi'_{\mathrm{el}} \mu_e \psi''_{\mathrm{el}} d\vec{r}$$

Hence

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

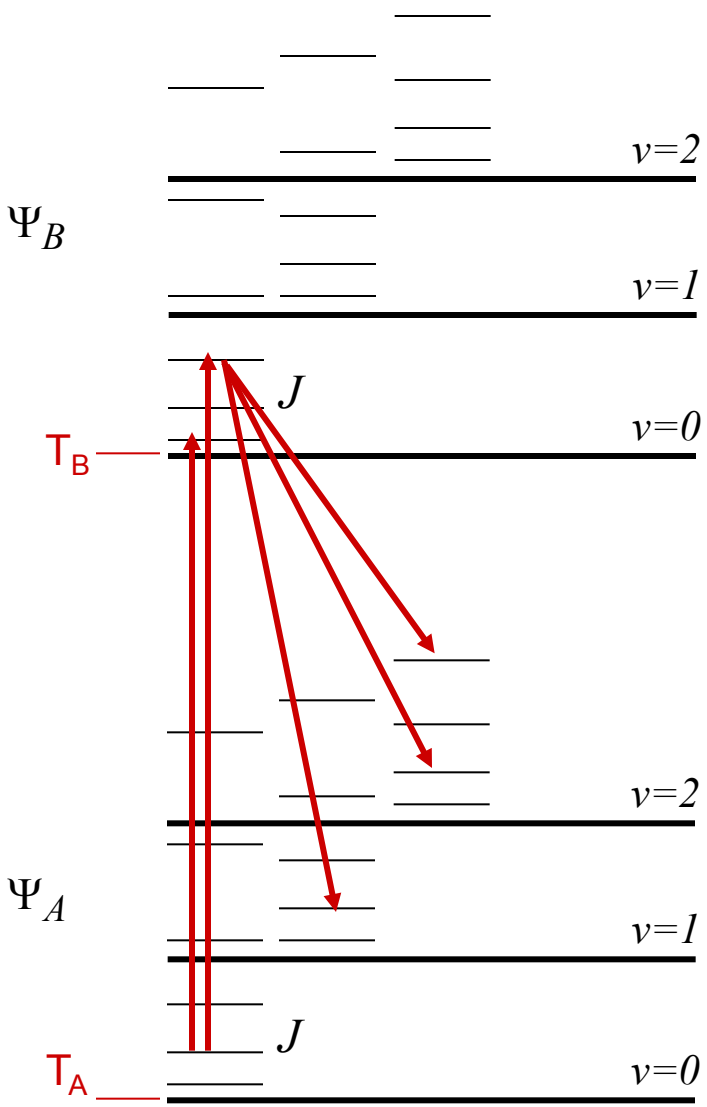
Intensity of electronic transitions

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



Intensity proportional to the square of the wave function overlap

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

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

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

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

H_2: only v=0 populated at "any" T

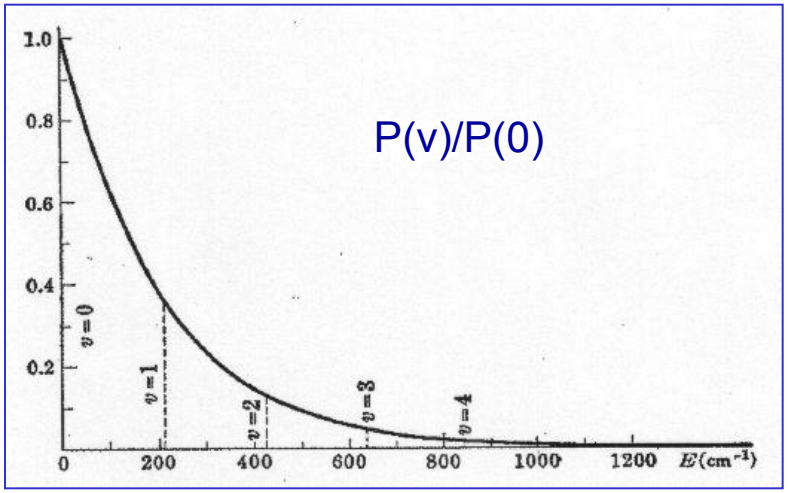


TABLE 14. RATIO OF THE NUMBER OF MOLECULES IN THE FIRST TO THAT IN THE ZEROTH VIBRATIONAL LEVEL FOR 300° K. AND 1000° K.

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

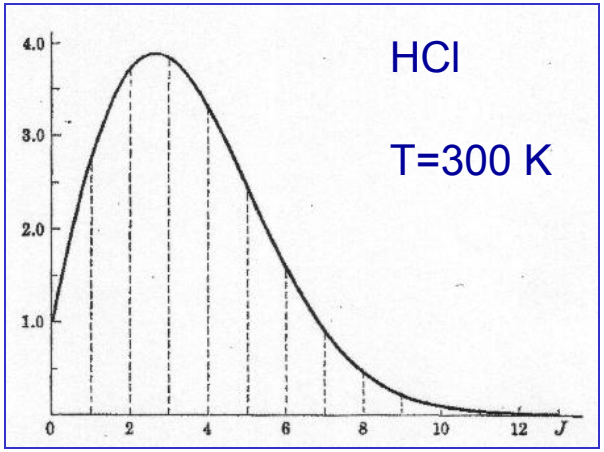
Probability of finding a molecule in a rotational quantum state:

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

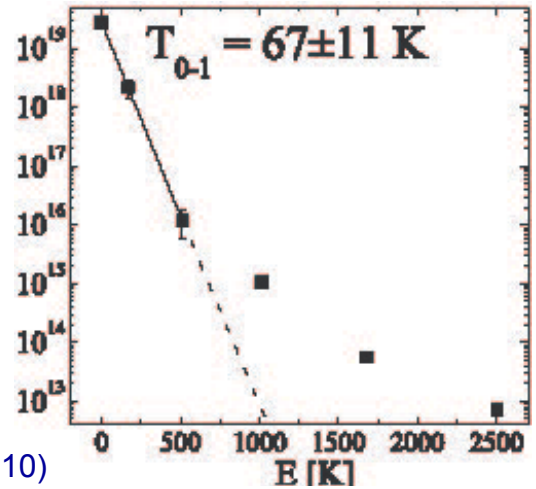
$$= \frac{1}{Z_{rot}}(2J+1)e^{-BJ(J+1)+DJ^2(J+1)^2}$$

Find optimum via

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



Boltzmann-plot H_2 in Q1232+082 Quasar
(Ivanchik MNRAS 2010)



Para and Ortho Hydrogen; nuclear spin

$\vec{I} = \vec{I}_1 + \vec{I}_2 \qquad M_I = m_{I_1} + m_{I_2}; \qquad I = 0,\ 1 \qquad M_S = -1,\ 0,\ 1$

$$|I=1, M_I=1\rangle = |\uparrow,\uparrow\rangle$$

$$|I=1, M_I=0\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow,\downarrow\rangle + |\downarrow,\uparrow\rangle\right)$$

$$|I=1, M_I=-1\rangle = |\downarrow,\downarrow\rangle$$

A triplet of symmetric
nuclear spin wave functions
(symmetry related to interchange)

$$|I=0, M_I=0\rangle = \frac{1}{\sqrt{2}}\left(|\uparrow,\downarrow\rangle - |\downarrow,\uparrow\rangle\right)$$

A singlet of an anti-symmetric
Nuclear spin wave function

Total wave function must be anti-symmetric for interchange of protons (Pauli principle):

Ortho-hydrogen: triply degenerate $\psi^A_{rot}\chi^S_{nuc-spin}$ $\longrightarrow$ Odd N-levels: $N=1,3,5$ …

Para-hydrogen: singly degenerate $\psi^S_{rot}\chi^A_{nuc-spin}$ $\longrightarrow$ Even N-levels: $N=0,2$ ..

Isotope effects in molecules; sensitivity for μ-variation

Electronic

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

$$\longrightarrow \quad \nabla_A \psi_{\mathrm{el}} \approx 0$$

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

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

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

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

So: $$K_\mu = -\frac{1}{2}$$

For ALL vibrational transitions / vibrational energies

Isotope effects in molecules; sensitivity for μ-variation

Rotational energy: $E_{\rm rot} = \hbar^2 \dfrac{N(N+1)}{2\mu R_e^2}$ $\qquad \nu = \dfrac{\hbar}{2\mu R_e^2}\left[N_2(N_2+1) - N_1(N_1+1)\right] = \dfrac{C}{\mu}$

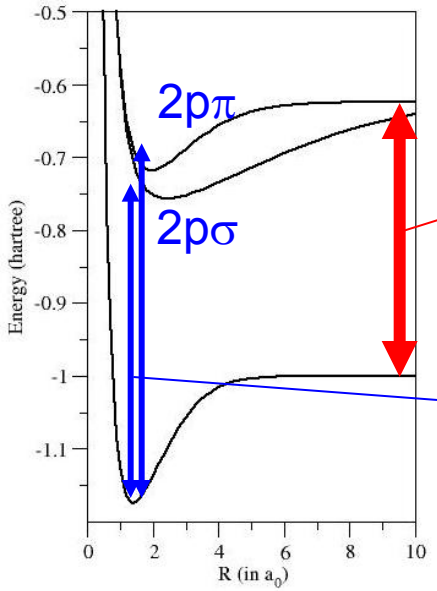
K-coefficient for purely rotational transition (or rotational energy):

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

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

Electronic spectra of H_2

H_2



H (Lyman-α) ~ 121 nm

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

THE
ASTROPHYSICAL JOURNAL
AN INTERNATIONAL REVIEW OF SPECTROSCOPY
AND ASTRONOMICAL PHYSICS

VOLUME XXIII APRIL 1906 NUMBER 3

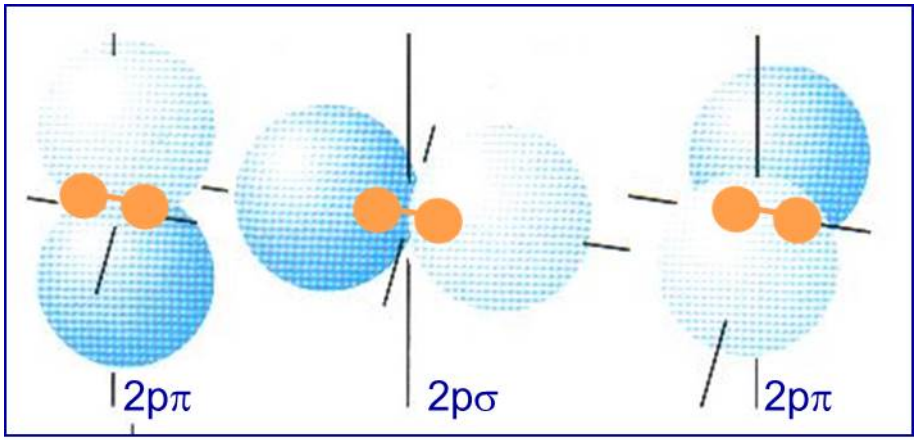
THE SPECTRUM OF HYDROGEN IN THE REGION OF EXTREMELY SHORT WAVE-LENGTH

By THEODORE LYMAN

Lyman and Werner band systems

$(1s)^2$- (1s)(2p)

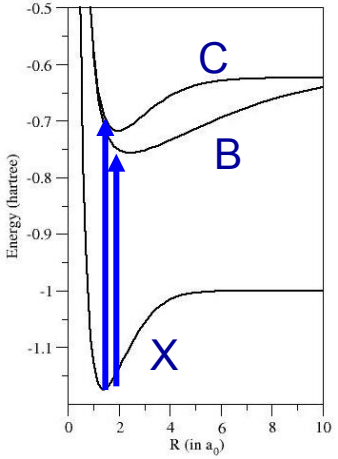
Threefold
2p orbitals



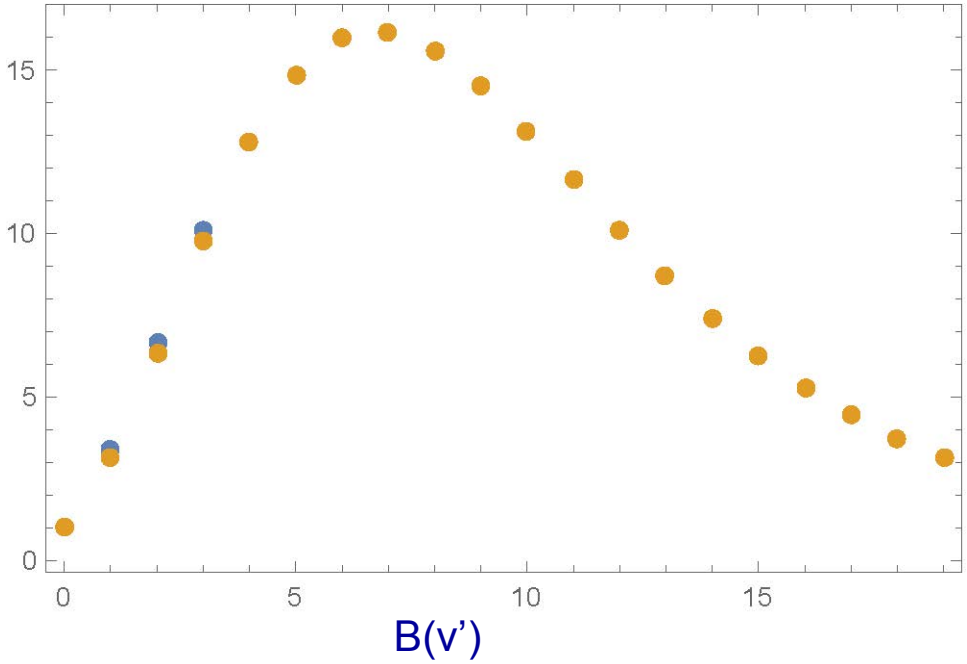
$X^1\Sigma_g^+$ - $(2p\sigma)$ $B^1\Sigma_u^+$

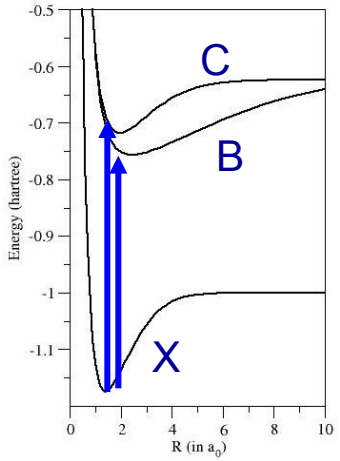
$X^1\Sigma_g^+$ - $(2p\pi)$ $C^1\Pi_u$

Doubly degenerate

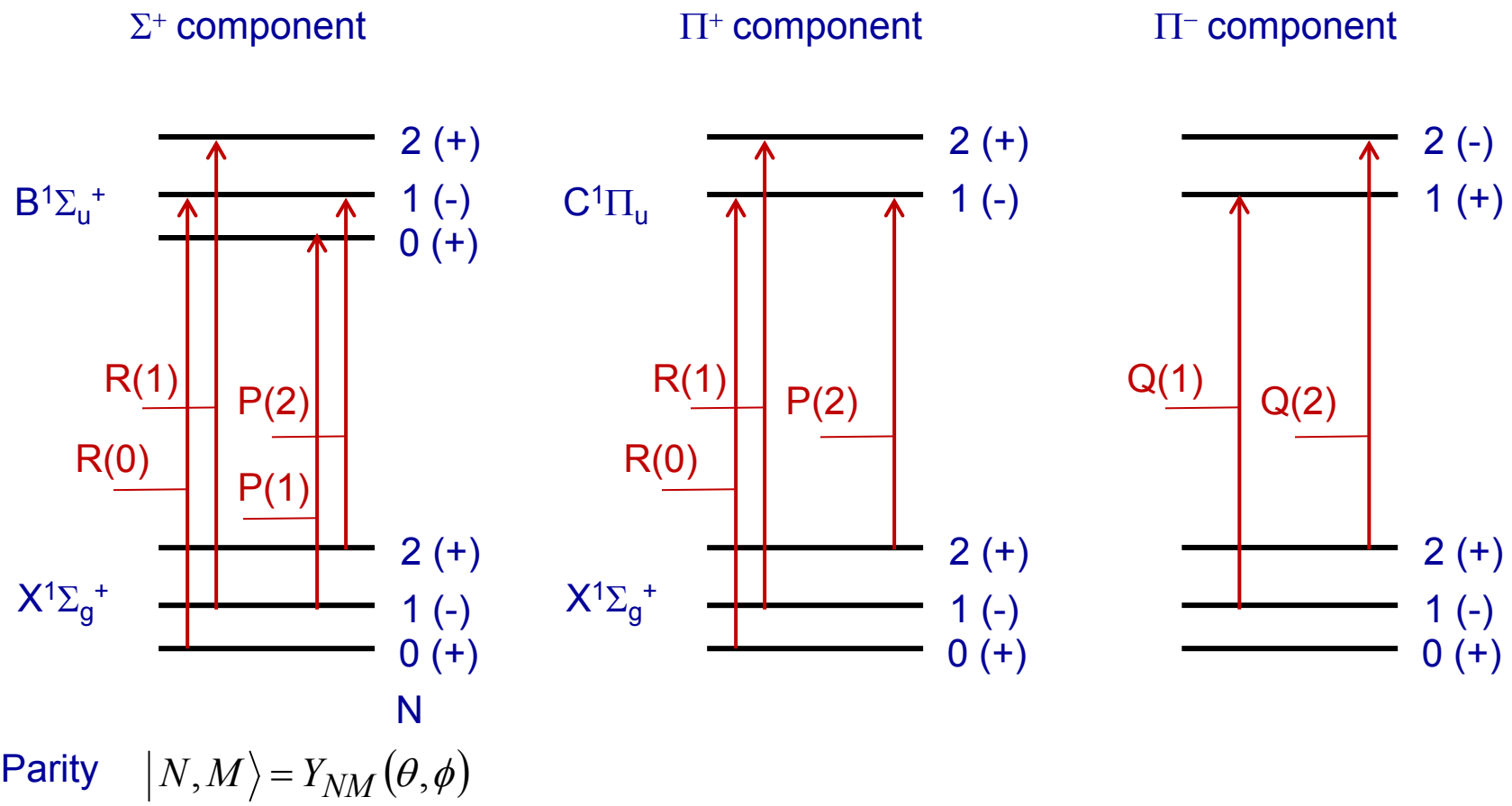


Franck-Condon Factors in H_2 absorption





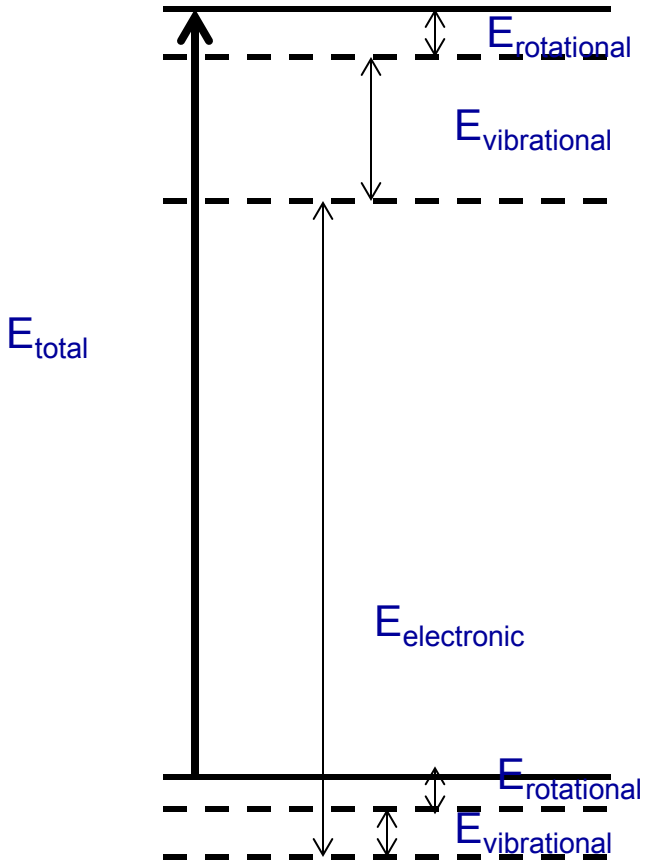
Lyman and Werner band systems



R, P, Q lines

Λ-doubling lifts degeneracy Π+ – Π− components
Rotation-electronic coupling (beyond BO)
Different parity

"Isotope effects" in molecules; sensitivity for μ-variation



Add contributions to sensitivity:

- Electronic
- Vibrational
- Rotational

In first order:

$$K_\mu = K_{elec}\frac{E_{elec}}{E_{tot}} + K_{vib}\frac{E_{vib}}{E_{tot}} + K_{rot}\frac{E_{rot}}{E_{tot}} = -\frac{1}{2}\frac{E_{vib}}{E_{tot}} - 1\frac{E_{rot}}{E_{tot}}$$

Dunham approach to sensitivity coefficients

$$K_i = -\frac{\mu}{E_e - E_g}\left(\frac{dE_e}{d\mu} - \frac{dE_g}{d\mu}\right)$$

Dunham representation:

$$E(v,J) = \sum_{k,l} Y_{kl}\left(v+\frac{1}{2}\right)^k [J(J+1)-\Lambda^2]^l$$

With known mass dependence:

$$Y_{kl} = A_{kl}\left(1+\frac{B_{kl}}{\mu}\right)\mu^{-(l+k/2)}$$

$$\frac{dY_{kl}}{d\mu} \approx -\frac{Y_{kl}}{\mu}\left(l+\frac{k}{2}+\frac{B_{kl}}{\mu}\right)$$

Results in:

$$\frac{dE(v,J)}{d\mu} = \sum_{k,l} \frac{dY_{kl}}{d\mu}\left(v+\frac{1}{2}\right)^k [J(J+1)-\Lambda^2]^l$$

Dunham coefficients $C^1\Pi^+_u$

Constant	Value	Constant	Value
Y_{00}	97916.14	Y_{10}	2444.3
Y_{20}	-69.6	Y_{30}	0.67
Y_{40}	-3.0×10^{-2}	Y_{01}	31.974
Y_{11}	-1.804	Y_{21}	0.274
Y_{31}	-9.0×10^{-2}	Y_{41}	9.0×10^{-3}
Y_{02}	-2.8×10^{-2}	Y_{03}	1.0×10^{-4}

Dunham coefficients $X^1\Sigma^+_g$

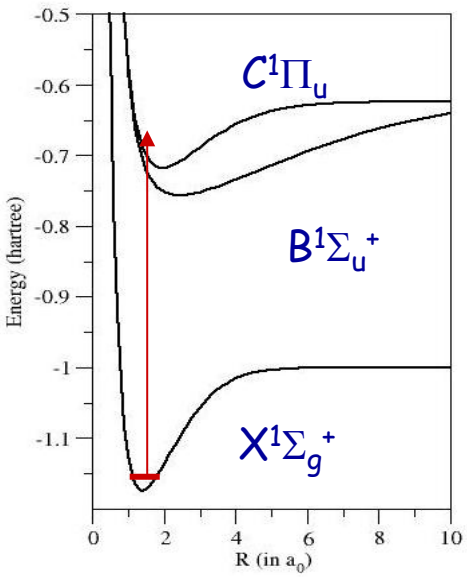
Constant	Value	Constant	Value
Y_{00}	-2169.69	Y_{10}	4399.37
Y_{20}	-120.2	Y_{30}	0.624
Y_{01}	60.82	Y_{11}	-2.994
Y_{21}	0.0223	Y_{02}	-0.046
Y_{12}	1.4×10^{-3}	Y_{03}	4.0×10^{-5}

Local perturbations; beyond Born-Oppenheimer

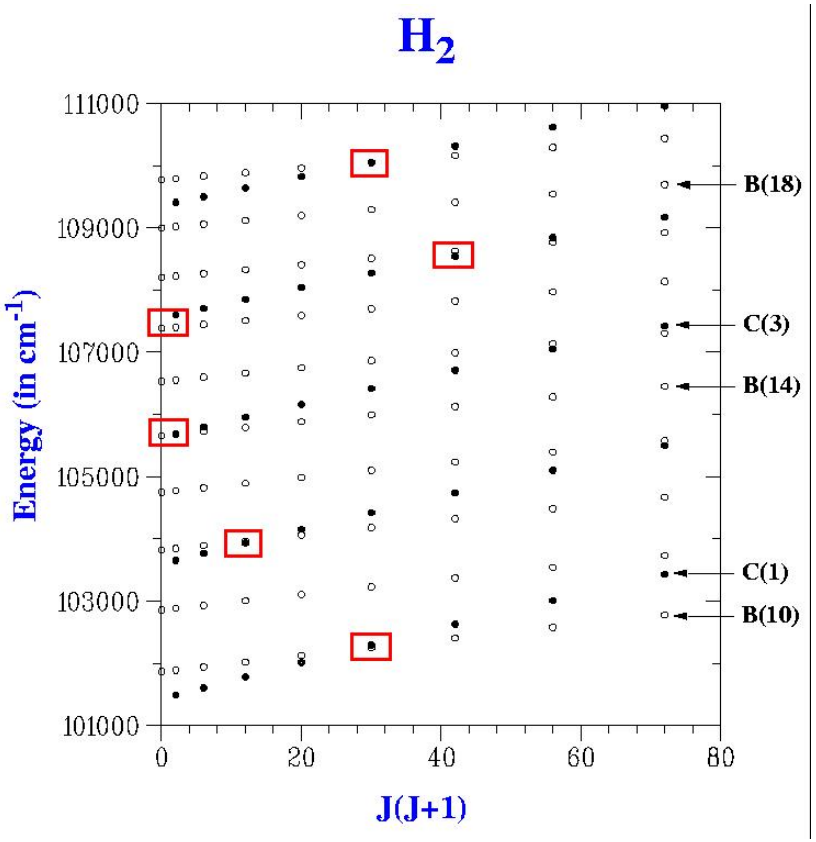
$$H' = J^{\pm} L^{\mp}$$

Matrix elements: $\left\langle B^1\Sigma_u^+, v_B, J, p \left| -\frac{\hbar^2}{2\mu R^2} J^+ L^- \right| C^1\Pi_u, v_C, J', p' \right\rangle$

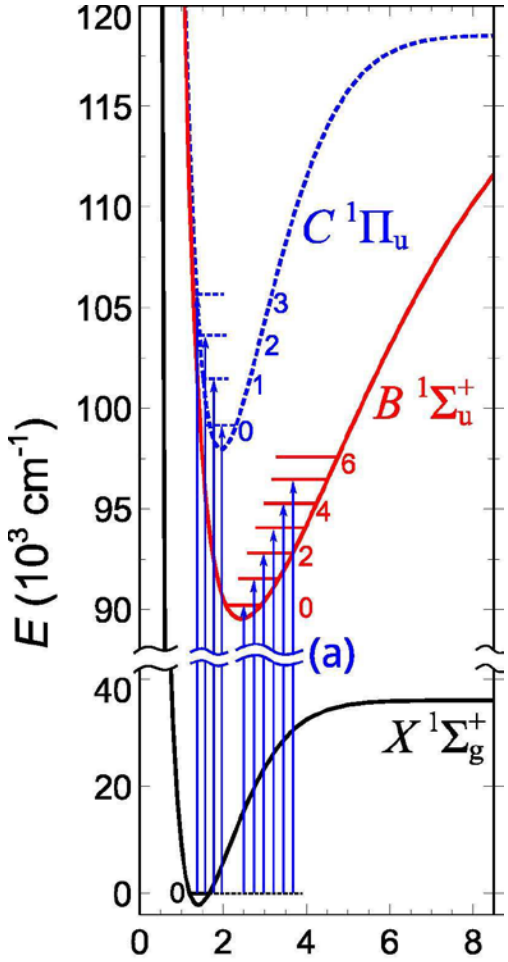
$$\begin{pmatrix} E_C(J) & H_{CB}\sqrt{J(J+1)} \\ H_{CB}\sqrt{J(J+1)} & E_B(J) \end{pmatrix}$$

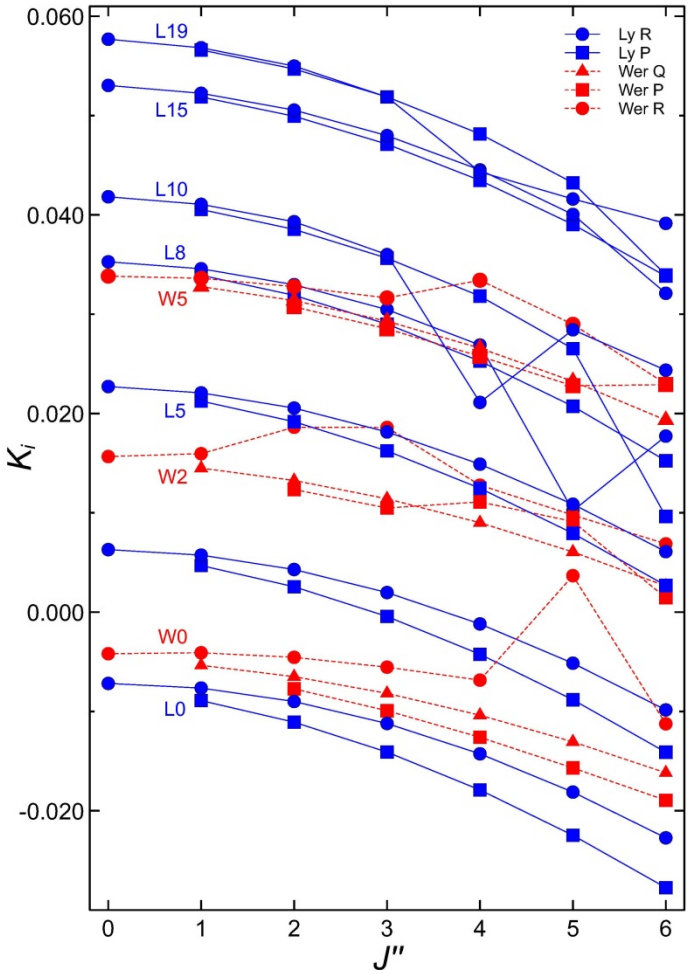


C(1) ⊗ B(10)
C(2) ⊗ B(12)
C(3) ⊗ B(14)
C(4) ⊗ B(17)



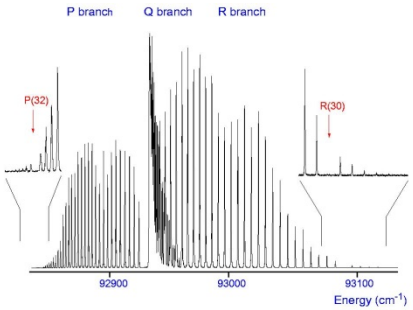
Lyman and Werner Bands; sensitivity for μ-variation



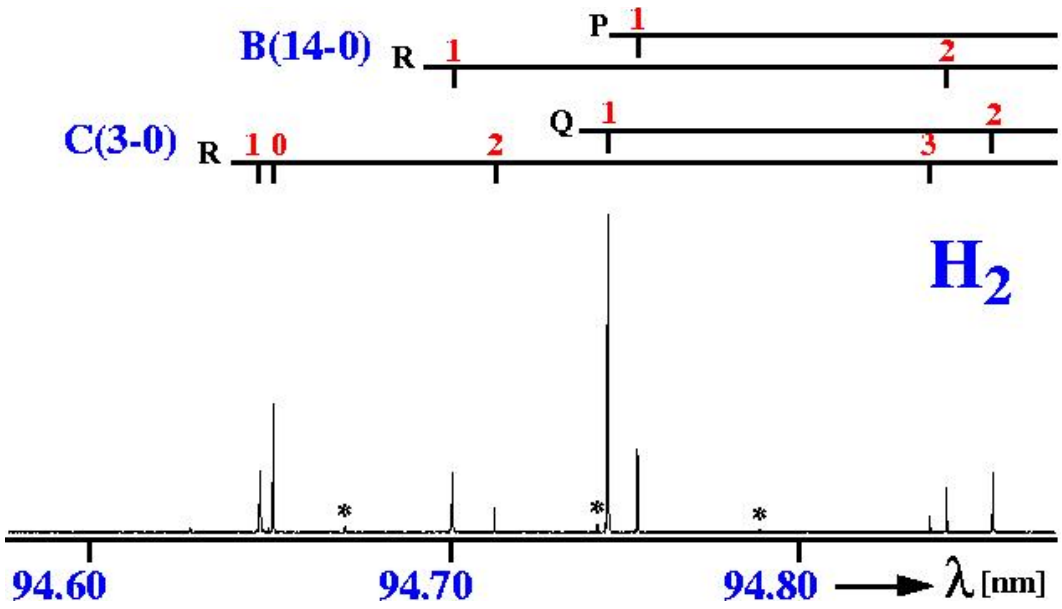


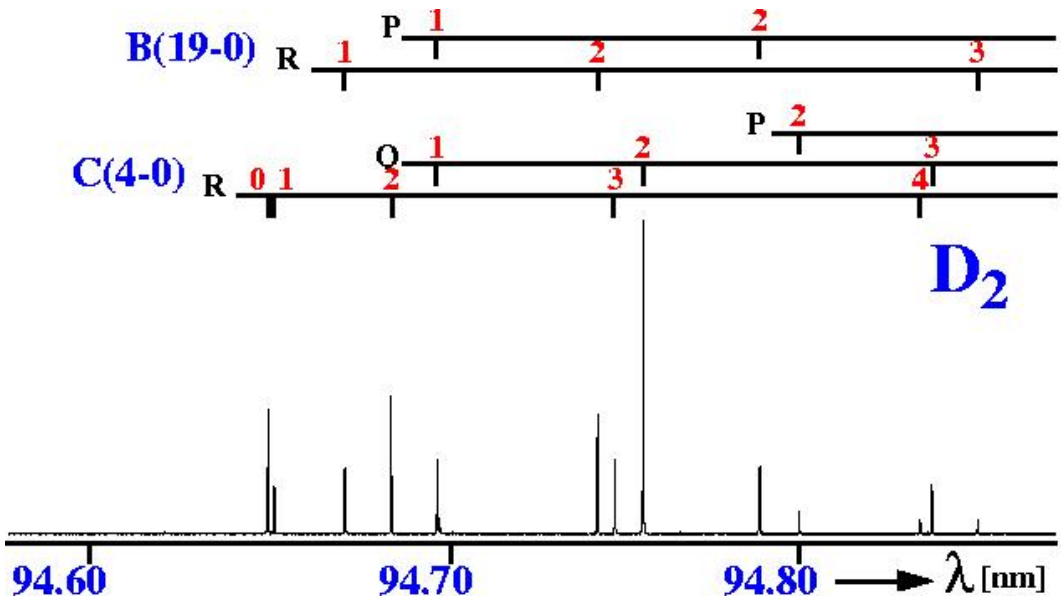
Laser spectrum

Hydrogen does not have
a “molecular band spectrum”

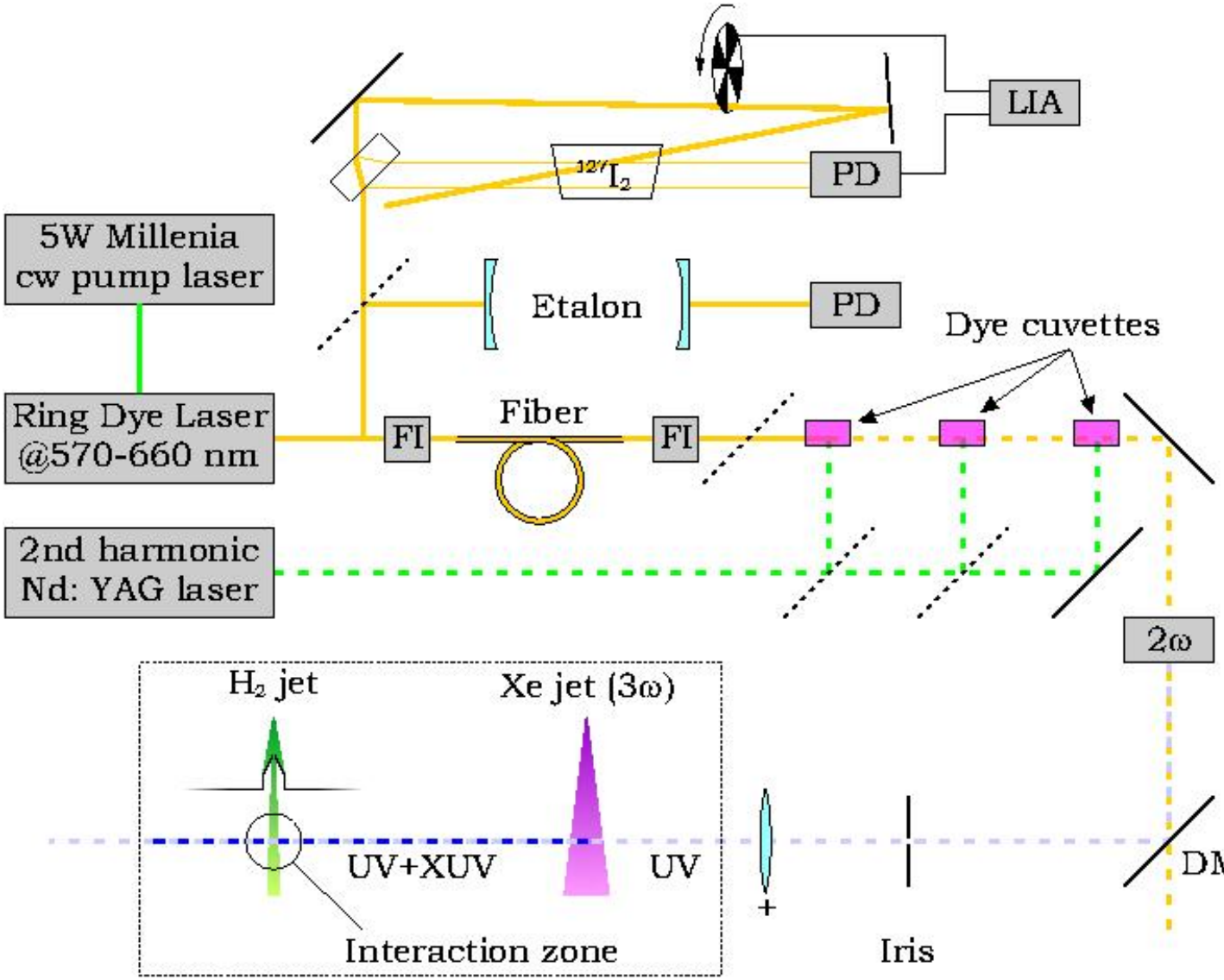


P. Hinnen, W. Ubachs et al.
Can. J. Phys 72, 1032 (1994)



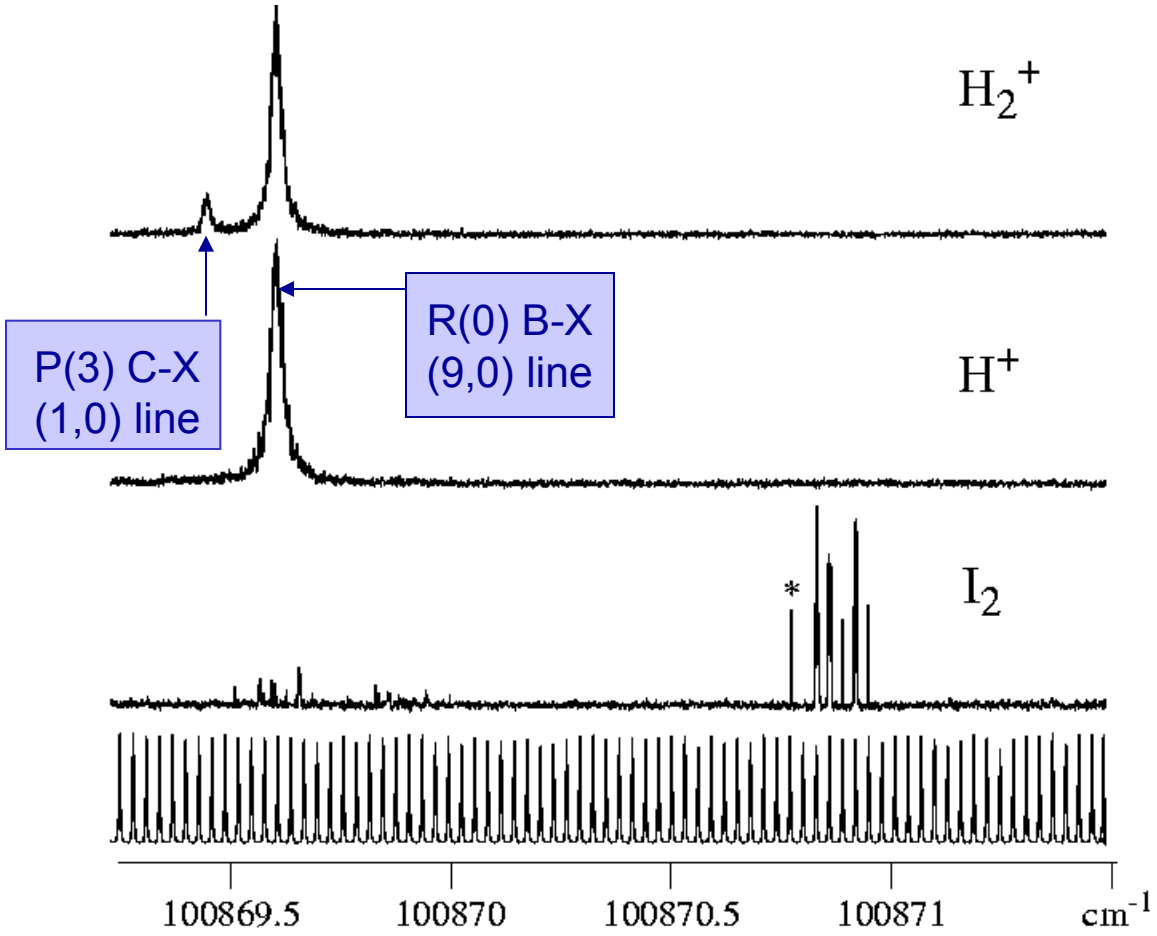


Precision measurements with tunable XUV laser



Pulsed Dye Amplifier

1 XUV + 1 UV REMPI spectroscopy



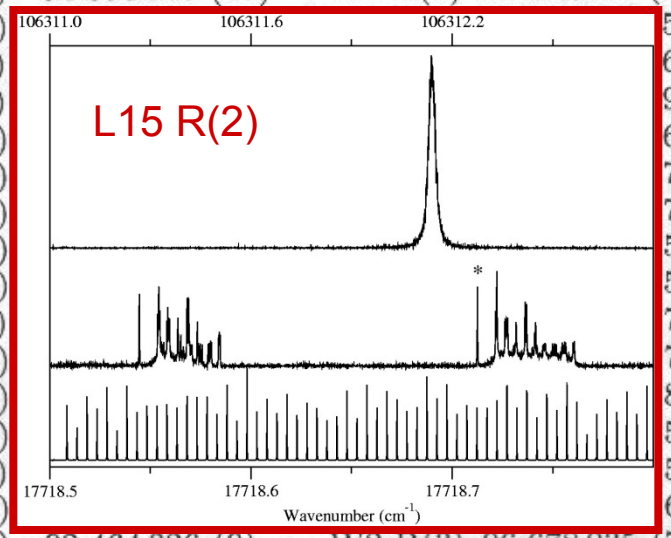
Evaluation of uncertainties:
Error budget

Residual Doppler	40 MHz
AC Stark	30 MHz
Freq chirp (PDA)	100 MHz
I_2 calibration	10 MHz
Statistical	30 MHz

Total (best lines): 0.005 cm^{-1}
0.000005 nm
5 x 10^{-8}

TABLE I: Comprehensive list of measured transition wavelengths of the Lyman (L) and Werner (W) lines using the ultra narrowband XUV laser source in Amsterdam. Values in nm.

Line	λ_0	Line	λ_0	Line	λ_0	Line	λ_0
L0 P(1)	111.006 251 (6)	L8 P(3)	100.838 615 (6)	L13 R(3)	95.894 665 (6)	W1 P(3)	99.138 046 (8)
L0 R(0)	110.812 733 (7)	L8 R(0)	100.182 387 (5)	L13 R(4)	96.215 297 (6)	W1 Q(1)	98.679 800 (5)
L0 R(1)	110.863 326 (7)	L8 R(1)	100.245 210 (5)	L14 P(1)	94.751 403 (10)	W1 Q(2)	98.797 445 (6)
L1 P(1)	109.405 198 (6)	L8 R(2)	100.398 545 (5)	L14 R(0)	94.616 931 (10)	W1 Q(3)	98.972 929 (8)
L1 P(2)	109.643 894 (6)	L8 R(3)	100.641 416 (6)	L14 R(1)	94.698 040 (10)	W1 R(0)	98.563 371 (5)
L1 P(3)	109.978 718 (7)	L9 P(1)	99.280 968 (5)	L14 R(2)			5)
L1 R(0)	109.219 523 (6)	L9 R(0)	99.137 891 (5)	L15 P(1)			6)
L1 R(1)	109.273 243 (6)	L9 R(1)	99.201 637 (5)	L15 P(3)			9)
L1 R(2)	109.424 460 (6)	L9 R(2)	99.355 061 (9)	L15 R(0)			6)
L1 R(3)	109.672 534 (6)	L9 R(3)	99.597 278 (20)	L15 R(1)			7)
L2 P(1)	107.892 547 (5)	L10 P(1)	98.283 533 (5)	L15 R(2)			7)
L2 R(0)	107.713 874 (5)	L10 P(2)	98.486 398 (5)	L15 R(3)			5)
L2 R(1)	107.769 894 (5)	L10 P(3)	98.776 882 (6)	L15 R(4)			5)
L2 R(2)	107.922 542 (6)	L10 R(0)	98.143 871 (5)	L16 P(1)			7)
L2 R(3)	108.171 124 (7)	L10 R(1)	98.207 427 (5)	L16 R(0)			7)
L2 R(4)	108.514 554 (6)	L10 R(2)	98.359 107 (5)	L16 R(1)			8)
L3 P(1)	106.460 539 (5)	L10 R(3)	98.596 279 (6)	L16 R(2)			5)
L3 P(2)	106.690 068 (5)	L11 P(1)	97.334 458 (5)	L17 P(1)			5)
L3 R(0)	106.288 214 (5)	L11 P(2)	97.534 576 (5)	L17 R(0)			6)
L3 R(1)	106.346 014 (5)	L11 P(3)	97.821 804 (6)	L17 R(1)	92.464 326 (9)	W2 R(3)	96.678 035 (7)
L3 R(2)	106.499 481 (5)	L11 R(0)	97.198 623 (5)	L18 P(1)	91.841 331 (9)	W3 P(2)	94.961 045 (5)
L3 R(3)	106.747 855 (5)	L11 R(1)	97.263 275 (5)	L18 R(0)			67 186 (5)
L4 P(1)	105.103 253 (4)	L11 R(2)	97.415 791 (5)	L18 R(1)			42 188 (5)
L4 R(0)	104.936 744 (4)	L11 R(3)	97.655 283 (6)	L18 R(2)			61 583 (5)
L4 R(1)	104.995 976 (4)	L11 R(4)	97.980 512 (7)	L19 P(1)			39 773 (5)
L4 R(2)	105.149 857 (5)	L11 R(5)	98.389 896 (7)	L19 P(2)			42 557 (4)
L4 R(3)	105.397 610 (4)	L12 P(1)	96.431 064 (5)	L19 P(3)	91.638 293 (34)	W3 R(1)	94.638 475 (4)
L5 P(1)	103.815 713 (4)	L12 P(2)	96.627 550 (5)	L19 R(0)	91.082 073 (17)	W3 R(2)	94.711 169 (4)
L5 R(0)	103.654 581 (4)	L12 P(3)	96.908 984 (6)	L19 R(1)	91.147 950 (17)	W3 R(3)	94.841 967 (5)
L5 R(1)	103.714 992 (4)	L12 R(0)	96.297 800 (5)	L19 R(2)	91.295 107 (17)	W3 R(4)	95.031 536 (5)
L5 R(2)	103.869 027 (4)	L12 R(1)	96.360 800 (5)	L19 R(3)	91.521 225 (17)	W4 P(2)	93.260 468 (10)
L5 R(3)	104.115 892 (4)	L12 R(2)	96.504 574 (5)	W0 P(2)	101.216 942 (6)	W4 P(3)	93.479 006 (10)
L6 P(1)	102.593 517 (8)	L12 R(3)	96.767 695 (6)	W0 P(3)	101.450 423 (6)	W4 Q(1)	93.057 708 (10)
L6 R(0)	102.437 395 (8)	L12 R(4)	97.083 820 (8)	W0 Q(1)	100.977 088 (5)	W4 Q(2)	93.178 086 (10)
L6 R(1)	102.498 790 (8)	L12 R(5)	97.488 649 (9)	W0 Q(2)	101.093 845 (6)	W4 Q(3)	93.357 794 (10)



162 lines measured at ~ 5 x 10^{-8}

Conclusion : H_2 dipole-allowed absorption spectrum

Lyman (B-X) and Werner bands (C-X) are the strong absorptions (1s – 2p)

Molecular database is available

λ_i – set of accurate wavelengths

K_i – set of sensitivity coefficients

f_i – set of line oscillator strengths (from ab initio theory)

Γ_i – set of damping coefficients (from ab initio theory)

To be used in astrophysical applications

Lectures ICTP Winter School on Optics 2016

Precision Spectroscopy of Molecular Hydrogen

and Physics Beyond the Standard Model

Wim Ubachs
LaserLaB, Vrije Universiteit Amsterdam

Part 2

Probe for a varying proton-electron mass ratio from H_2

Empirical search for a change in μ

Compare H_2 in different epochs

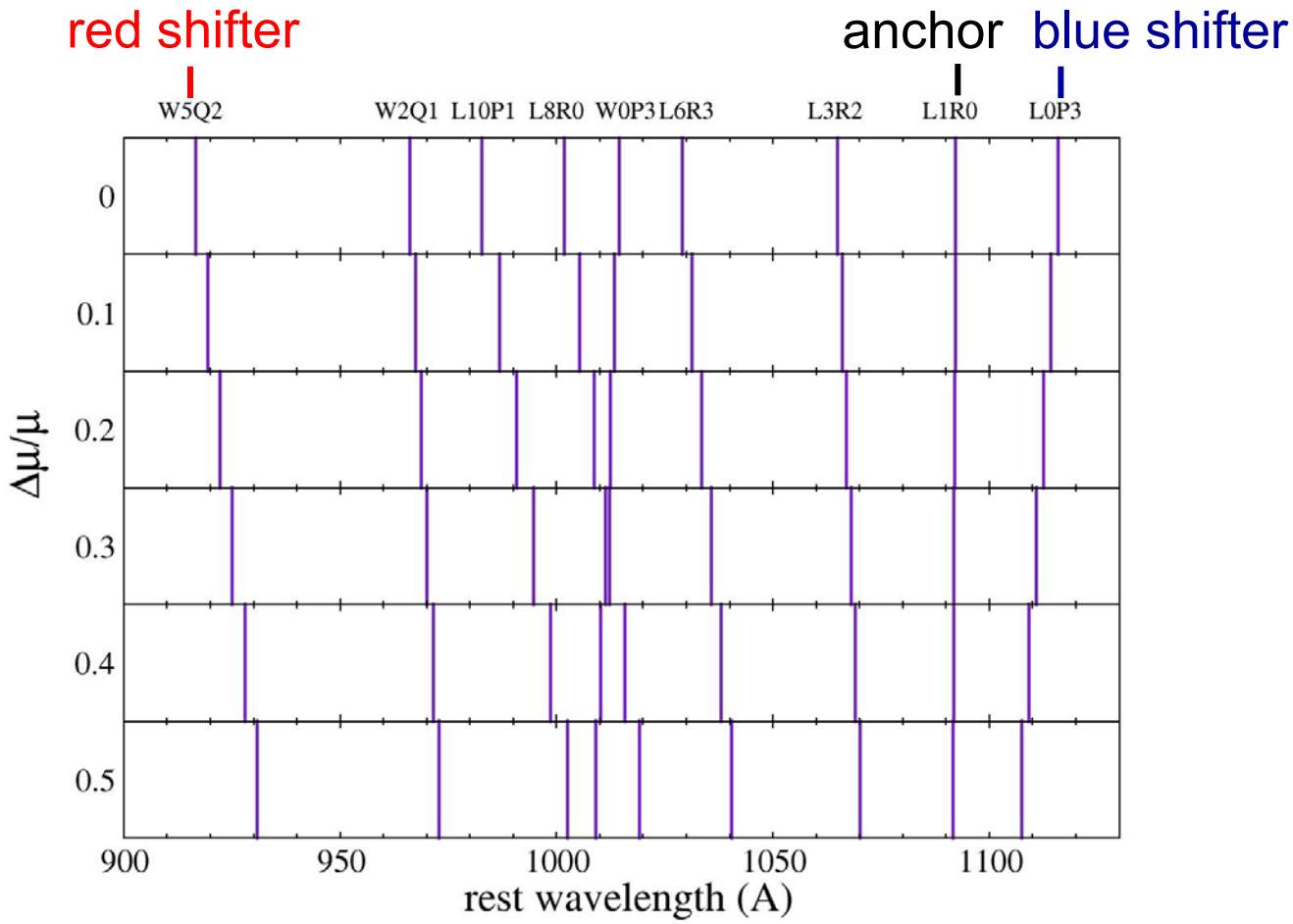
$$\frac{\lambda_i^z}{\lambda_i^0} \equiv 1 + z_i$$

Cosmological redshift

$$T = T_0\left[1 - \frac{1}{(1+z_{abs})^{3/2}}\right]$$

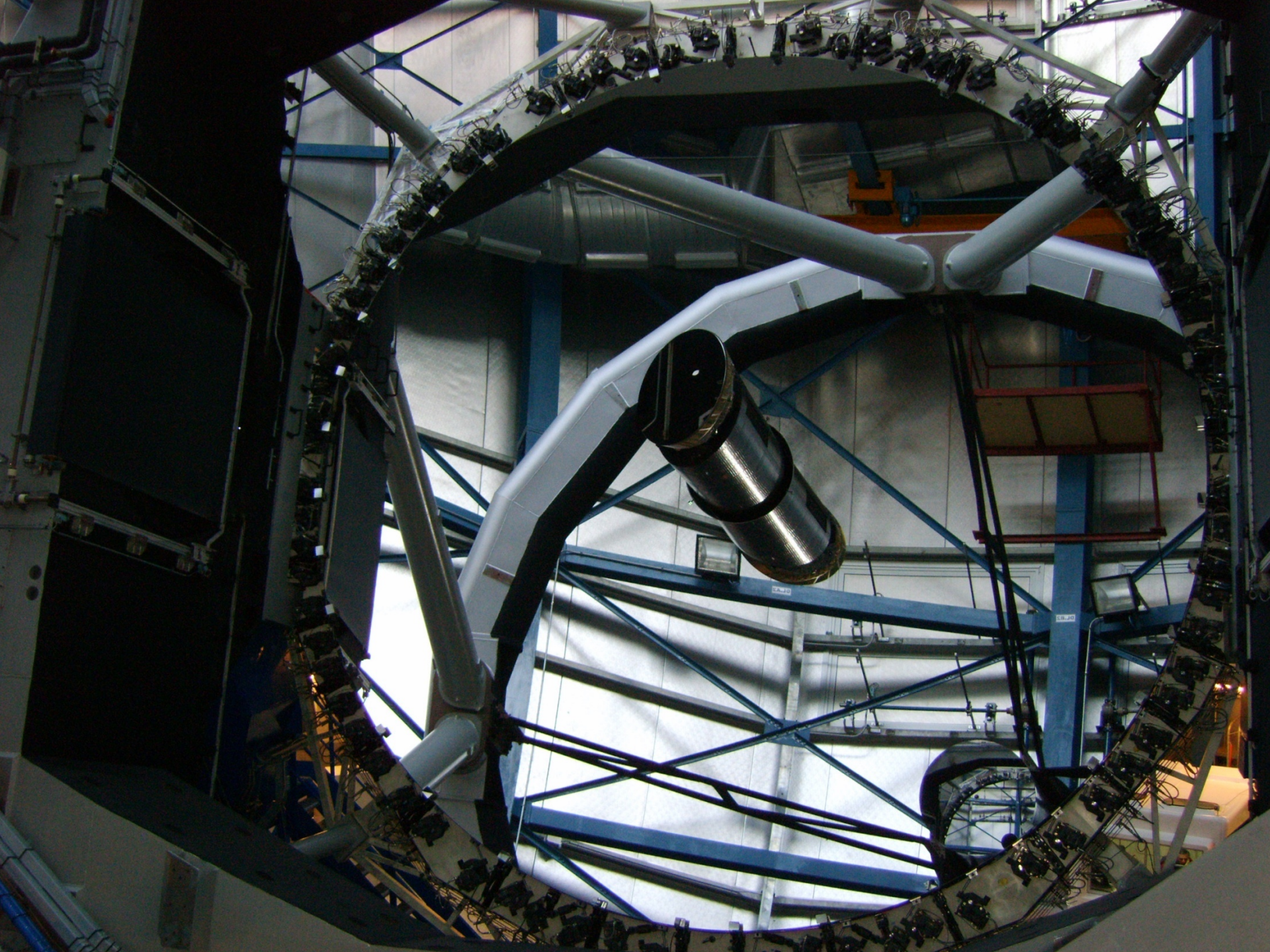
Practical: atmospheric transmission only for $z>2$

Sensitivity of H_2

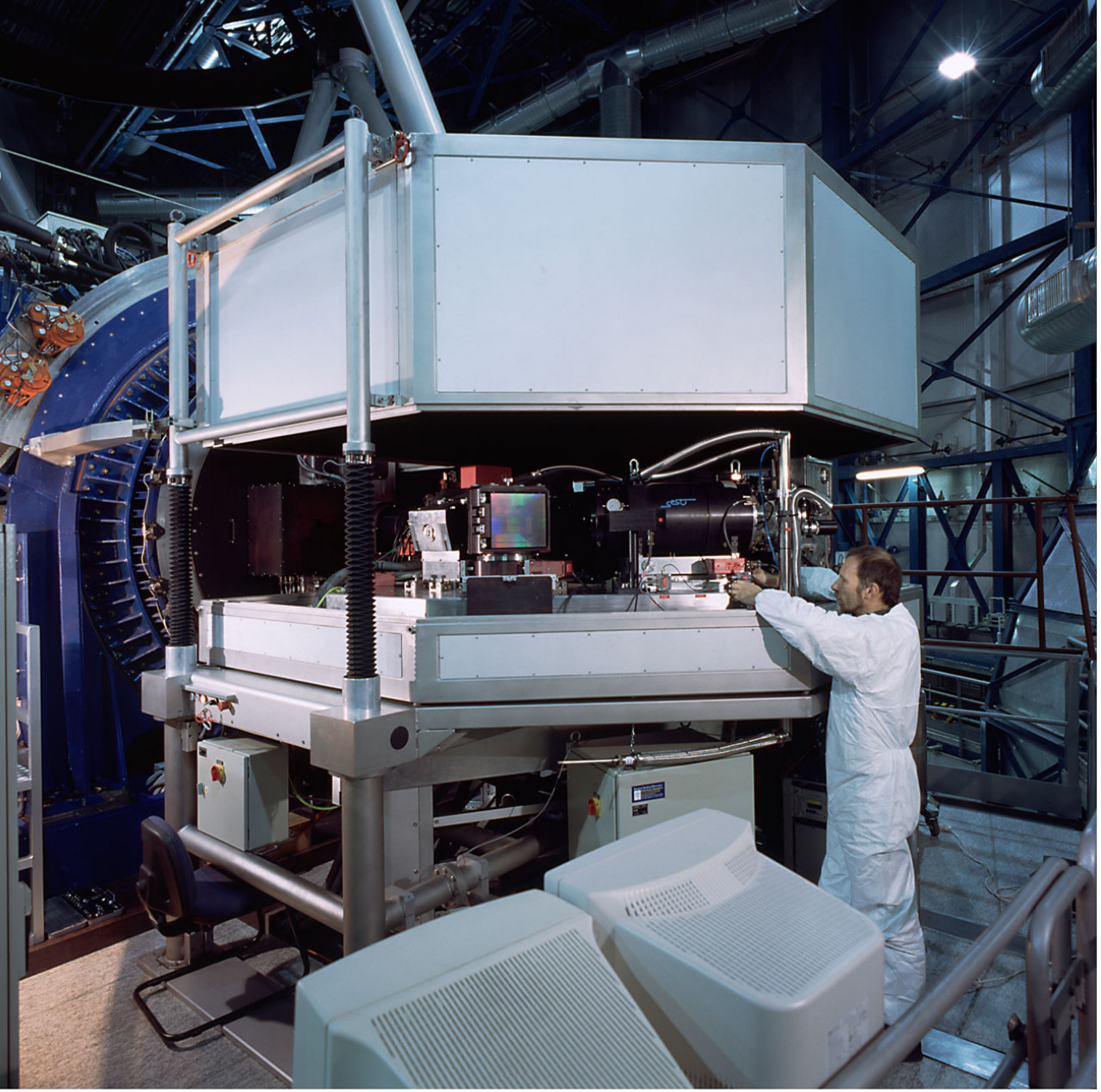


VLT – UVES
Paranal, Chili

Keck – HIRES
Hawaii




Q2348-011
z = 2.42
Magnitude
18.4
1 arcsecond
ESO-VLT
2007

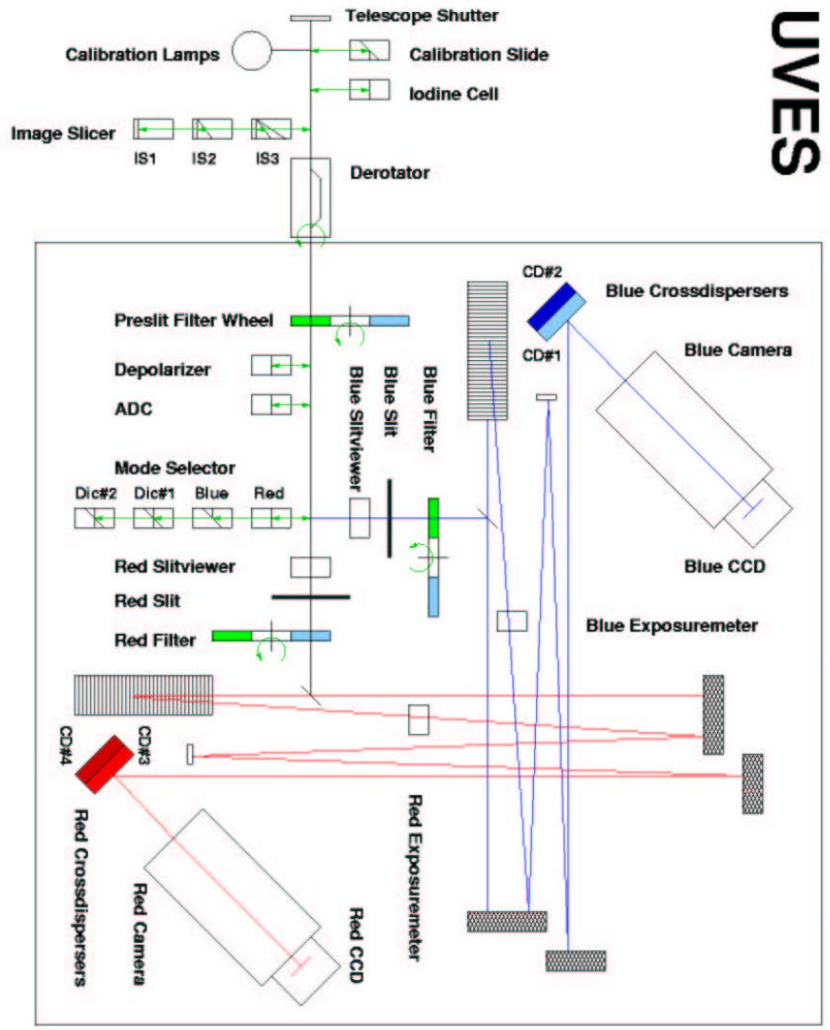


UVES at Kueyen

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

UVES: Ultraviolet – Visual Echelle Spectrograph

Calibration with UVES



Blue chip: 300-500 nm

Red chips: 420-1100 nm

Photon management

Standard calibration:

Comparison QSO exposure vs ThAr lamp exposure

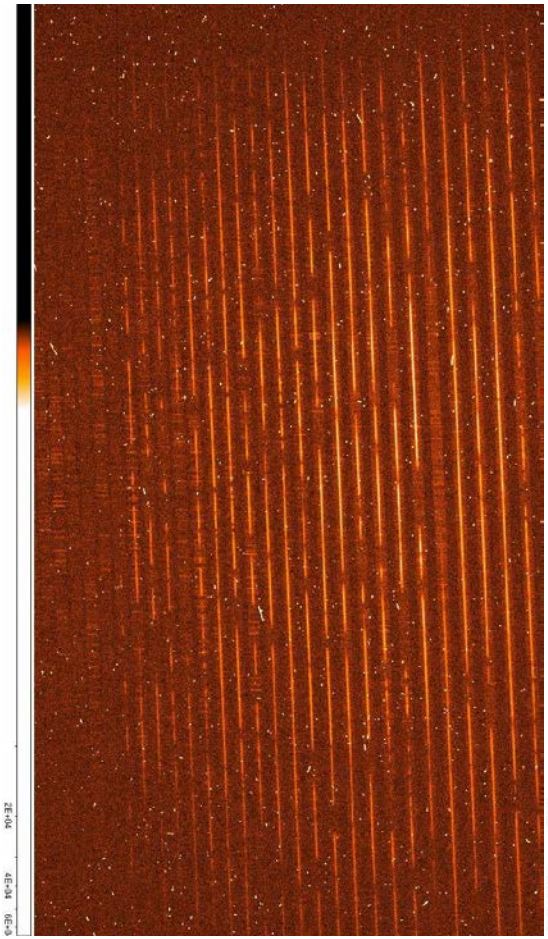
(Attached / Non-attached)

Problems:

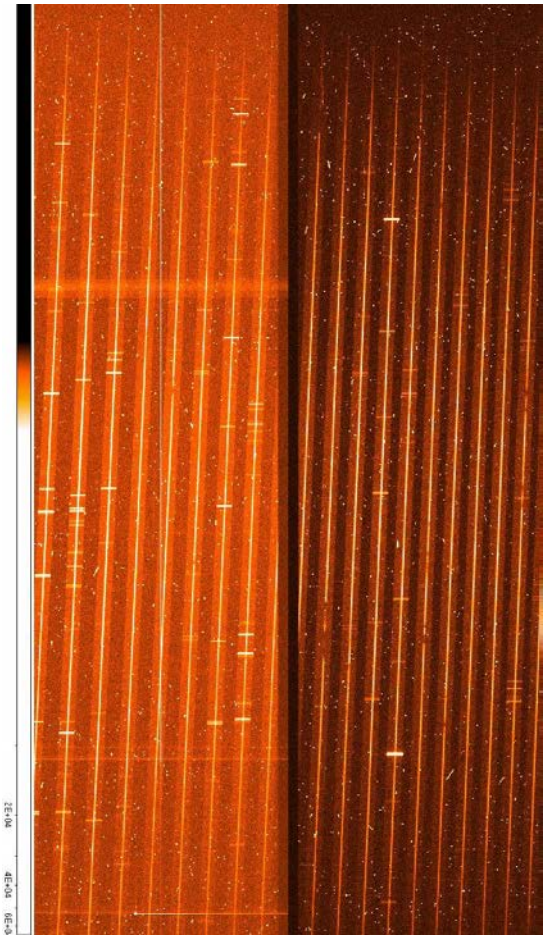
1. Different light path in spectrograph
2. Uniform illumination of slit
3. Red and blue parts of spectrum recorded on different CCDs

Systematic effects may mimic a $\Delta\mu/\mu \neq 0$!

Dispersion of Echelle Orders on to CCDs

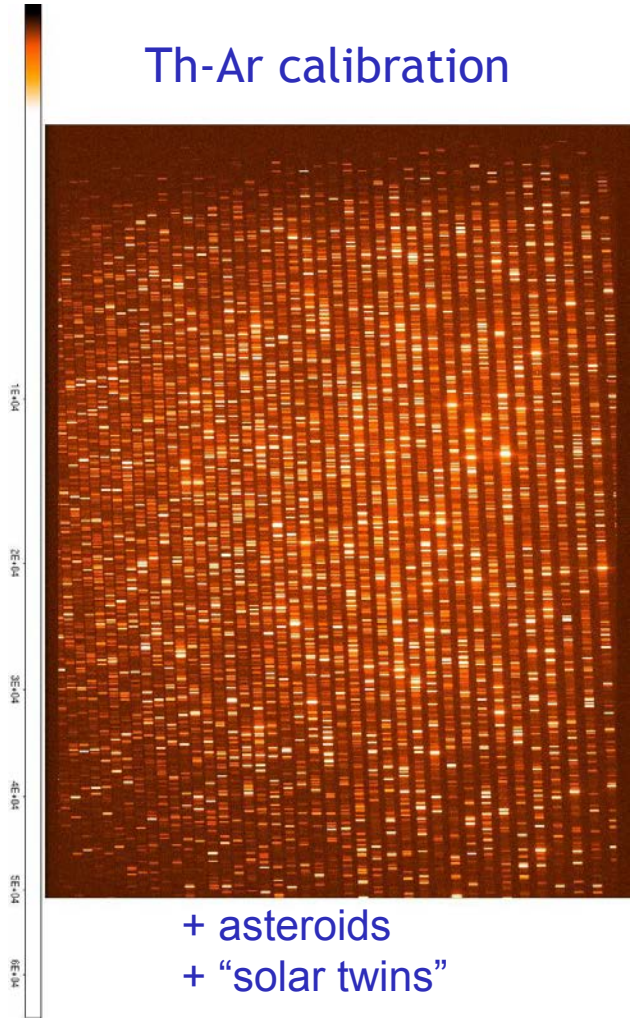


Blue chip



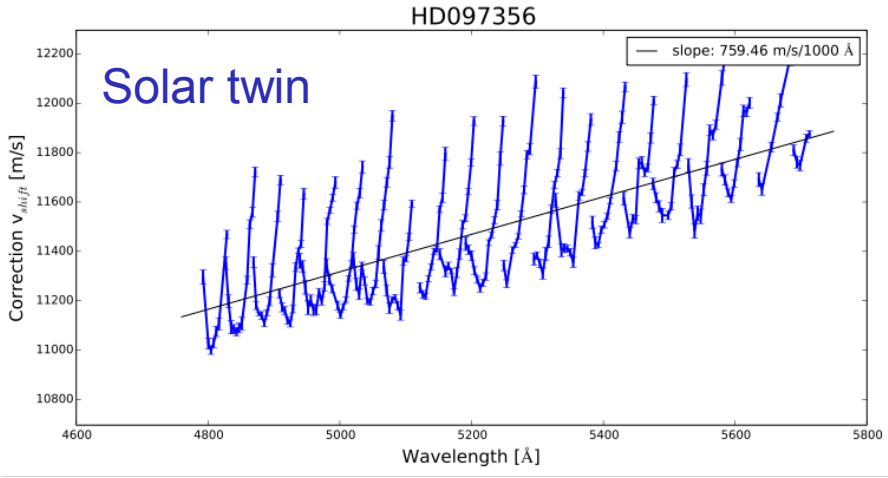
Two red chips

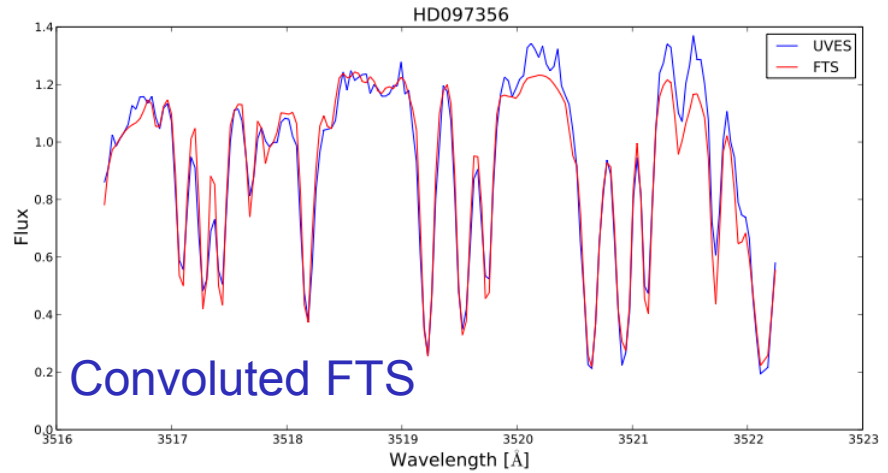
Th-Ar calibration



+ asteroids
+ “solar twins”

Supercalibrations





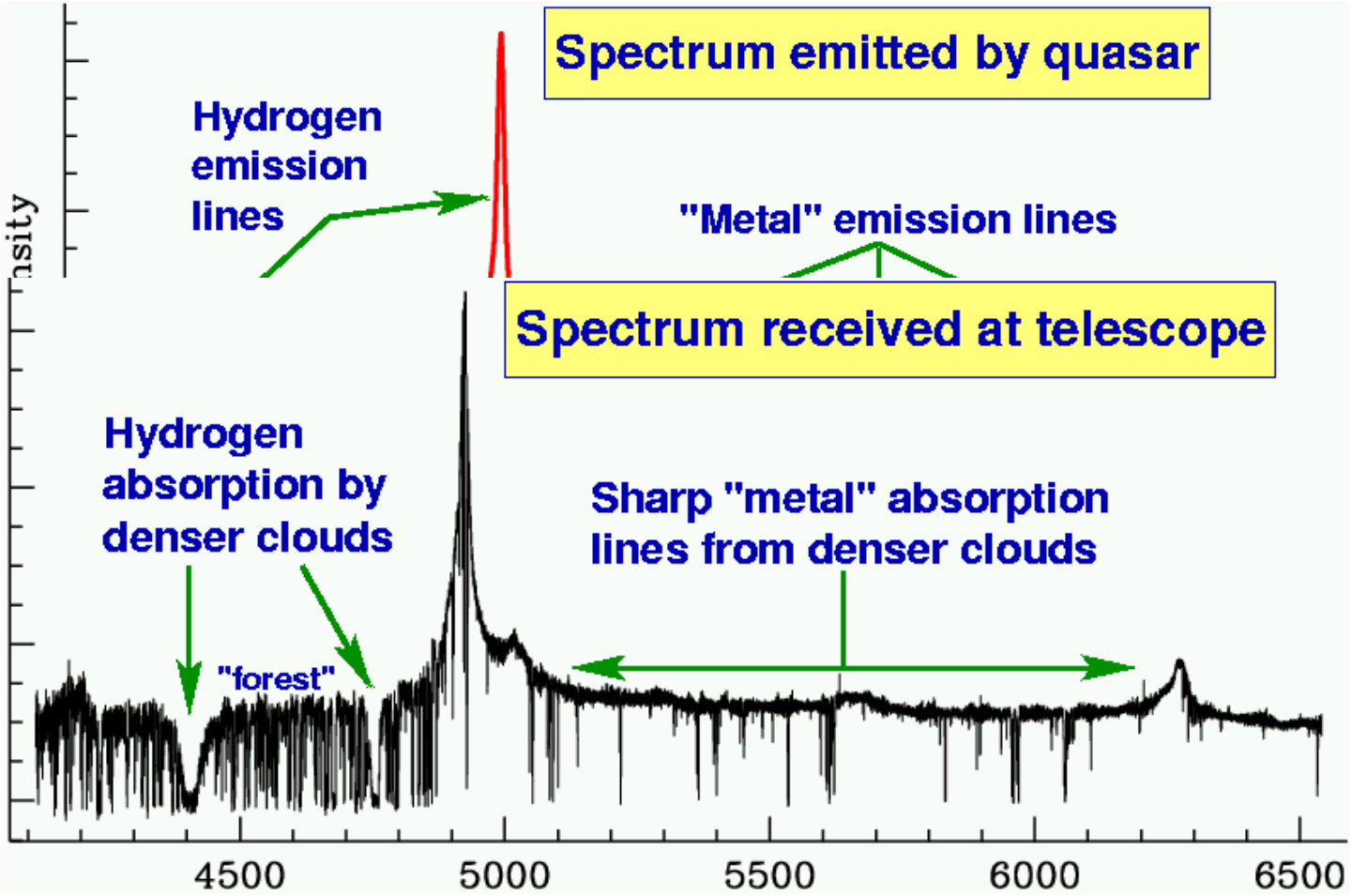
Long-range wavelength distortions

Rahmani et al. MNRAS 435 (2013) 861
Whitmore & Murphy MNRAS 447 (2015) 446

Asteroids and 'Solar Twins' targets

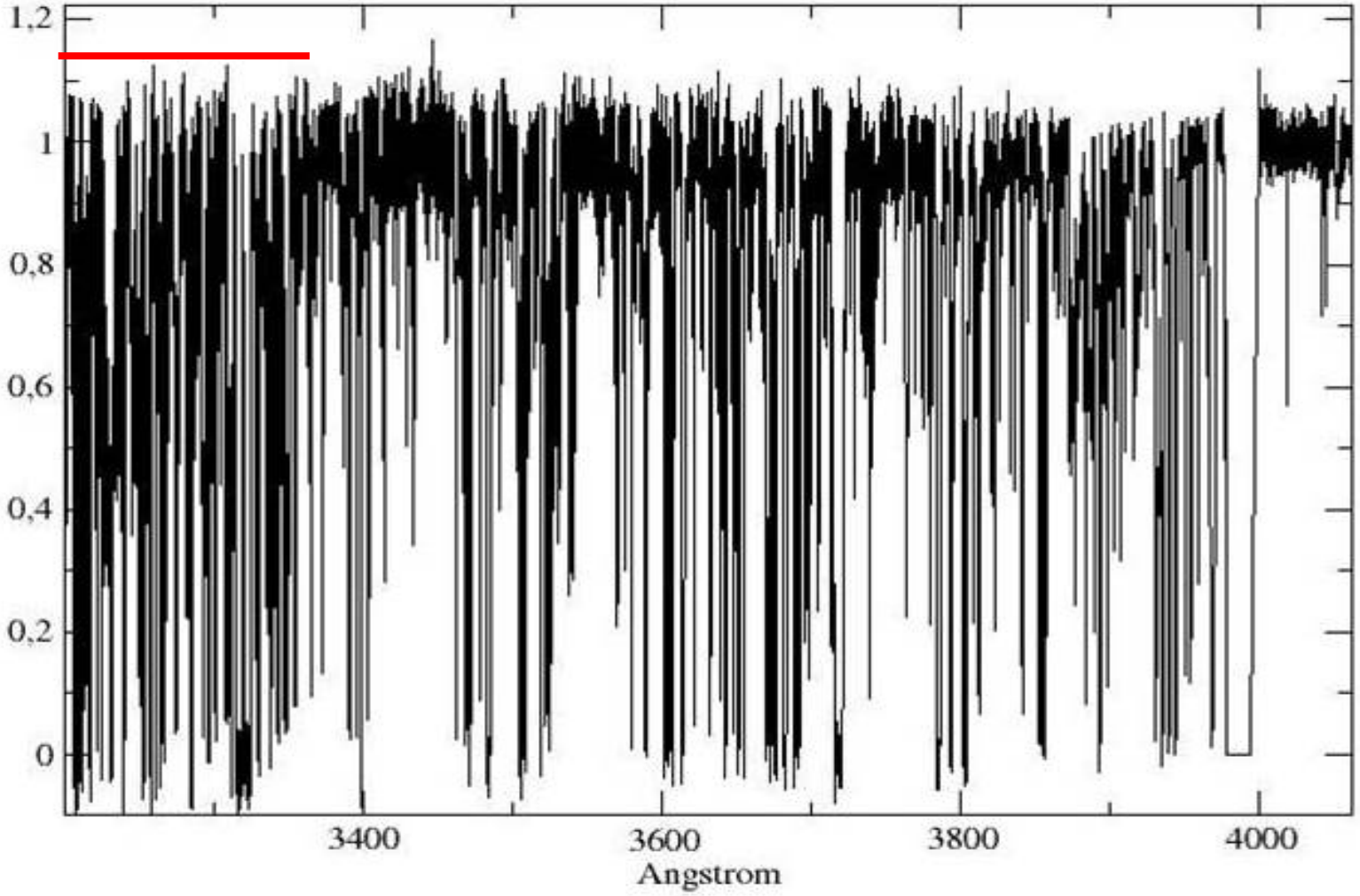
ThAr calibrated spectrum vs FTS spectrum

Linear slope correction

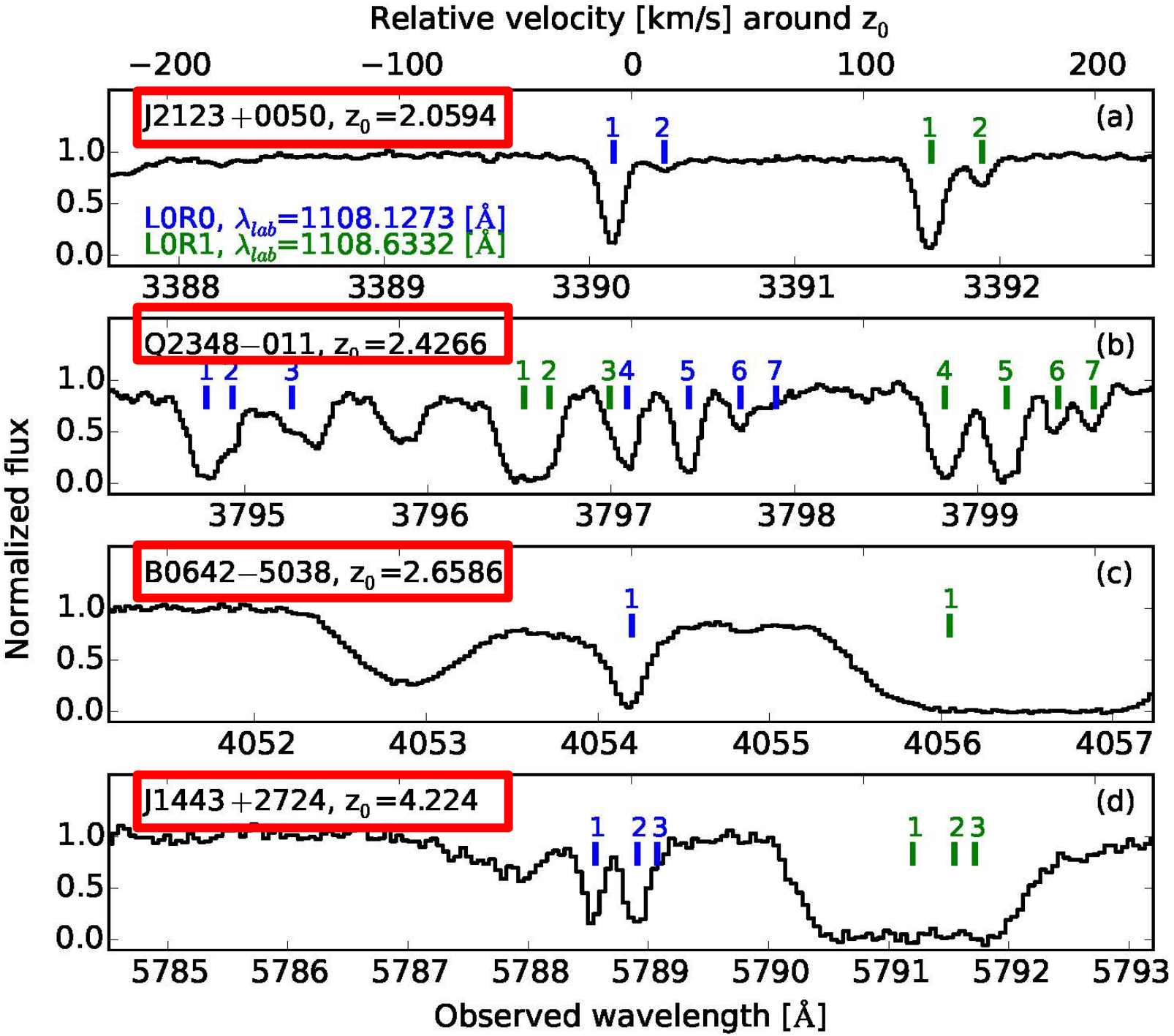

Spectrum emitted by quasar
Hydrogen emission lines
"Metal" emission lines
Spectrum received at telescope
Hydrogen absorption by denser clouds
Sharp "metal" absorption lines from denser clouds
"forest"
4500
5000
5500
6000
6500

J2123-005 from HIRES-Keck at Hawaii

Resolution 110000 ; z_{abs}=2.0593



Various systems observed



Analysis method: “comprehensive fitting”

Produce molecular fingerprint

λ_i – set of accurate wavelengths

f_i – set of line oscillator strengths (from ab initio theory)

Γ_i – set of damping coefficients (from ab initio theory)

Astrophysical conditions

b – Doppler width parameter

z – red shift

N_J – column densities

Fit equation onto spectrum
“Treat” HI and metal lines
Multiple velocity components (?)

$$\frac{\lambda_i^z}{\lambda_i^0} \equiv 1 + z_i = (1 + z_{abs})\left(1 + K_i \frac{\Delta\mu}{\mu}\right)$$

K_i – set of sensitivity coefficients

The best system: J2123-005 at z_{abs}=2.05

Unique spectrum from Keck; Resolution 110000 ; seeing 0.3"

Spectrum from VLT; R=54000; seeing 0.8"; better SNR

37 panels, 3071 – 3421 Å

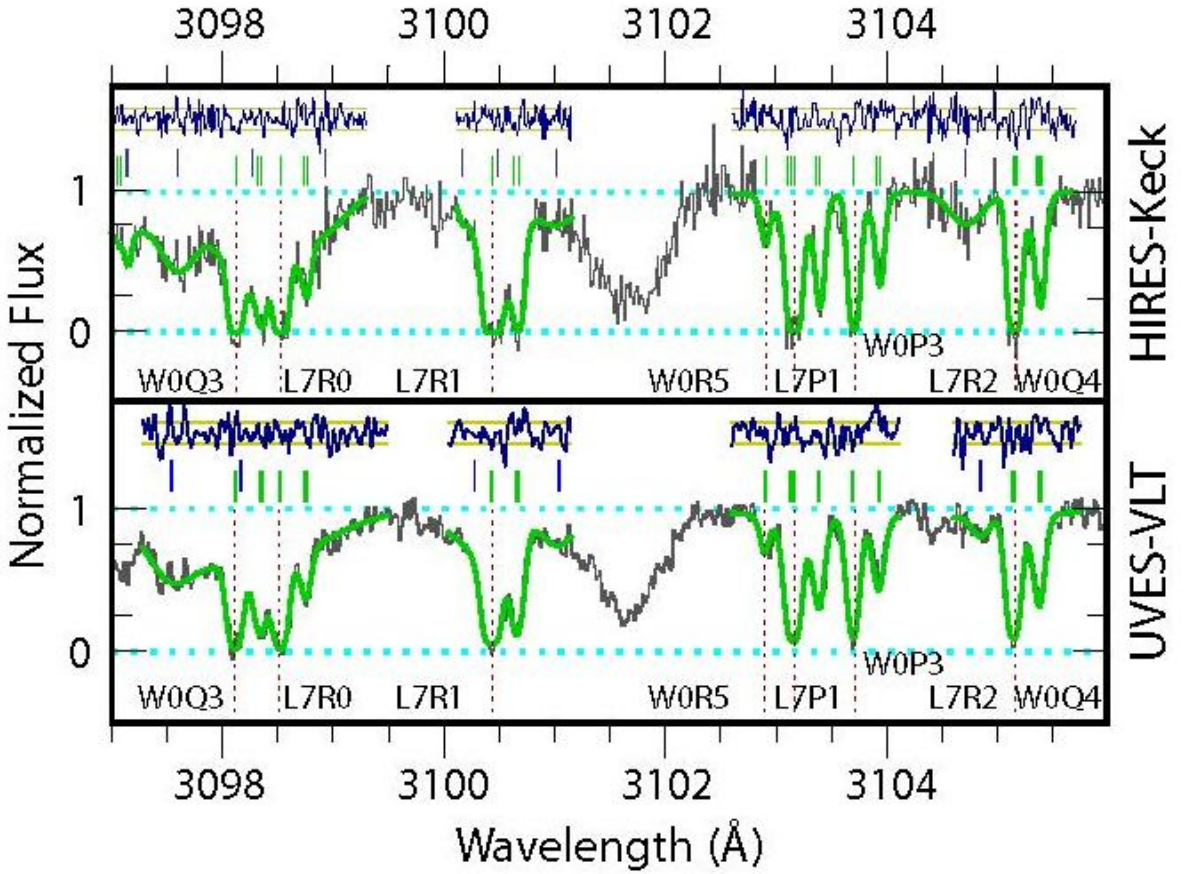
~100 H_2 + 7 HD lines

Keck:

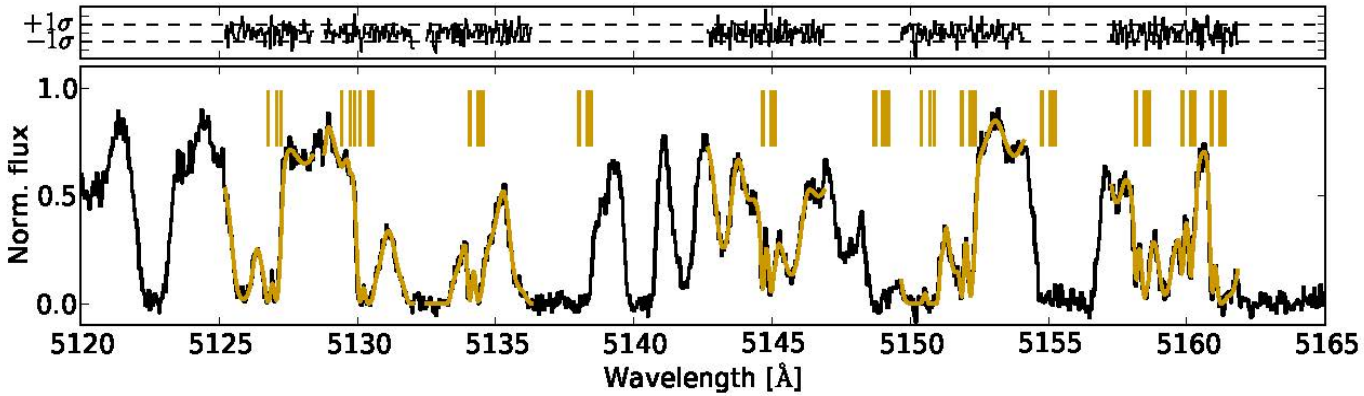
$\Delta\mu/\mu = (5.6 \pm 5.5_{stat} \pm 2.9_{syst}) \times 10^{-6}$

VLT:

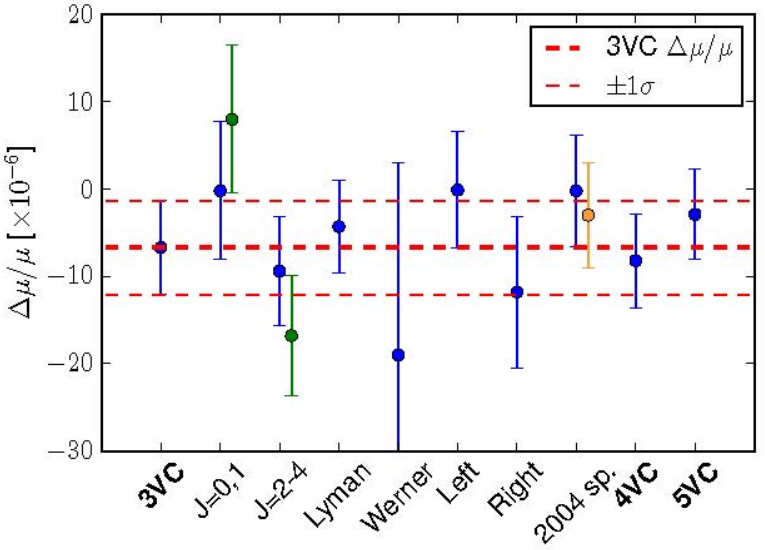
$\Delta\mu/\mu = (8.5 \pm 3.6_{stat} \pm 2.2_{syst}) \times 10^{-6}$



Q1441+272 ; the most distant
z_{abs} = 4.22 ; 1.5 Gyrs after the Big Bang



Systematic analysis



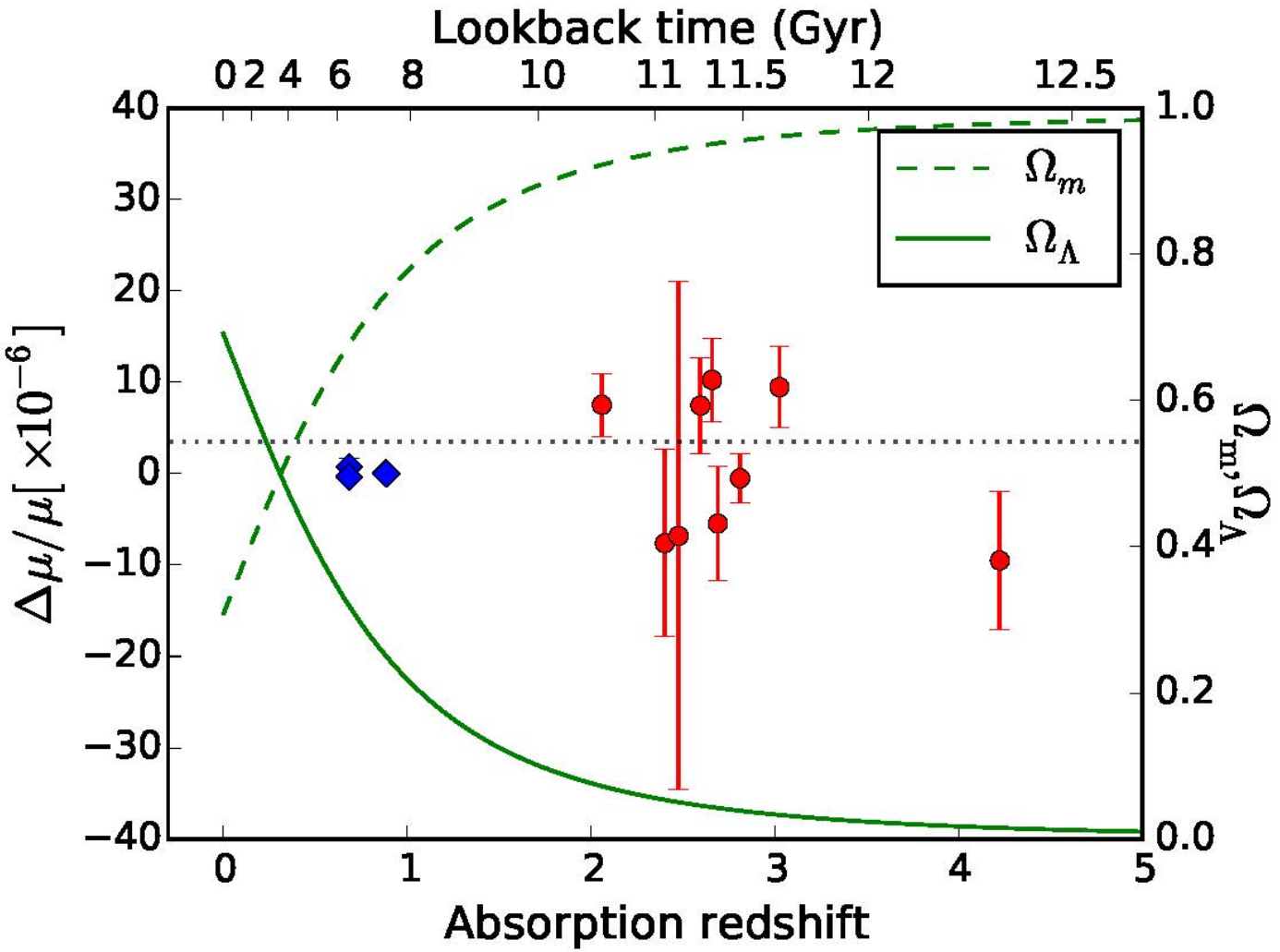
Phys. Rev. Lett. 114, 071301 (2015)

Limited H_2 absorbers 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]	→ Rahmani
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]	Done
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]	Done (+ 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]	Done
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

Status of cosmological μ-variation

Varying constants and the ratio Ω_m, Ω_Λ $|\Delta\mu/\mu| = (3.1 \pm 1.6) \times 10^{-6}$

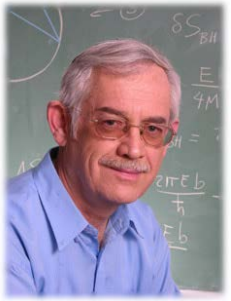


Varying Constants ?

Coupling constants are free parameters in Standard Model

Bekenstein-Barrow –Sandvik – Mageijo – Light scalar fields ϕ

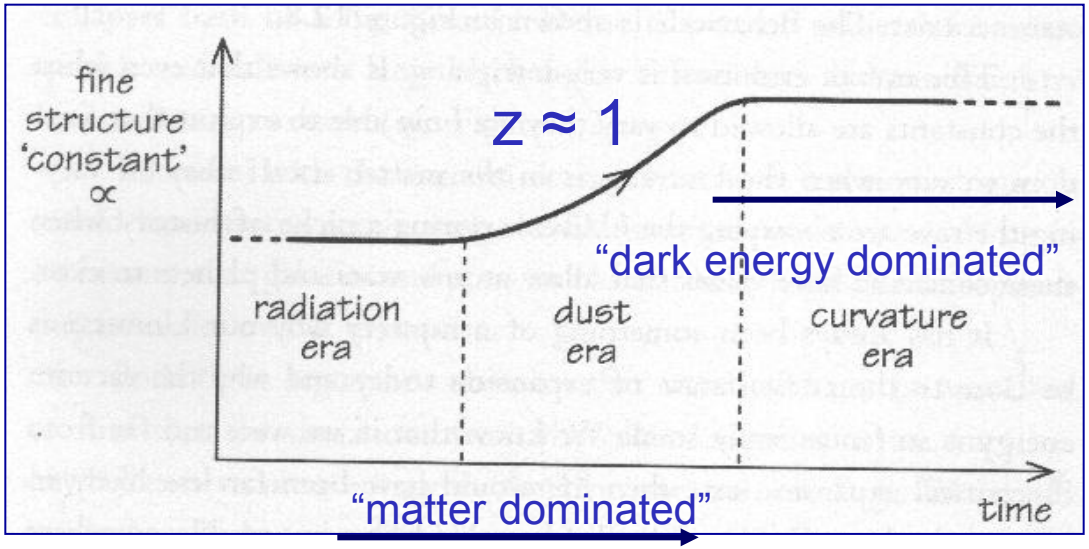
$$S = \int \left(L_{mat} + \frac{j_\mu}{c} A^\mu - \frac{\varepsilon_0}{4} F_{\mu\nu} F^{\mu\nu} e^{-2\phi} - \frac{\hbar c}{2l^2} \partial_\mu \phi \partial^\mu \phi \right) d\Omega$$



Jacob Bekenstein

1) Coupling to cosmology
Variation on cosmological time scales

2) Coupling to matter density -> “chameleons”
Coupling to gravity



Hydrogen nearby; white dwarf stars in our galaxy

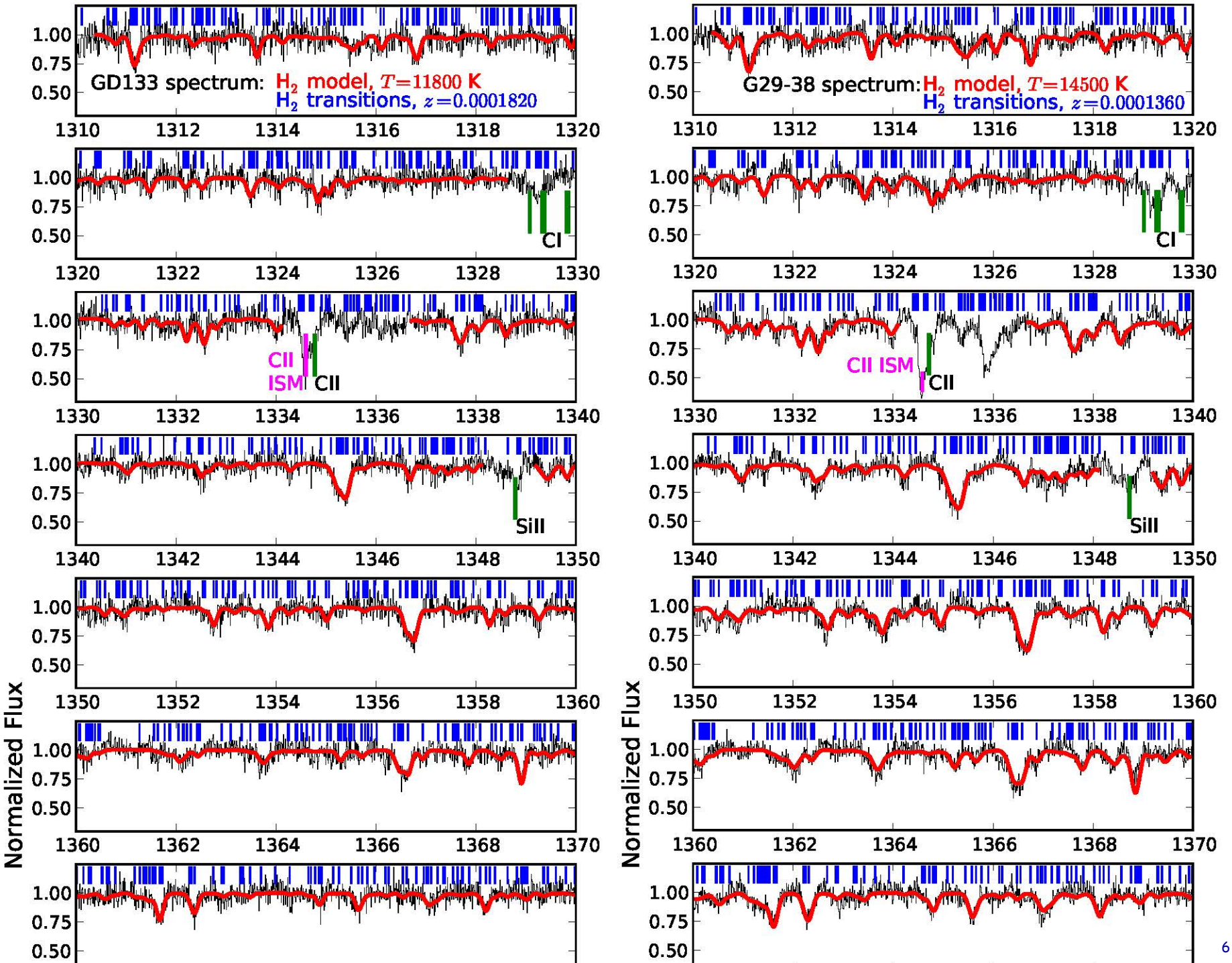
Dependence of $\Delta\mu/\mu$ on gravitational field

Spectrum of GD-133 and GD29-38
White Dwarf stars

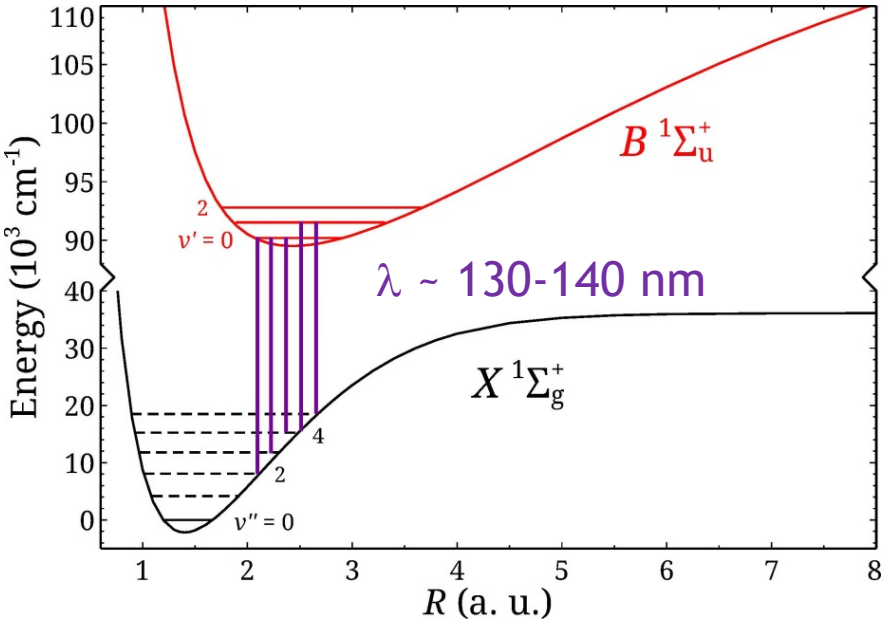
H_2 in VUV

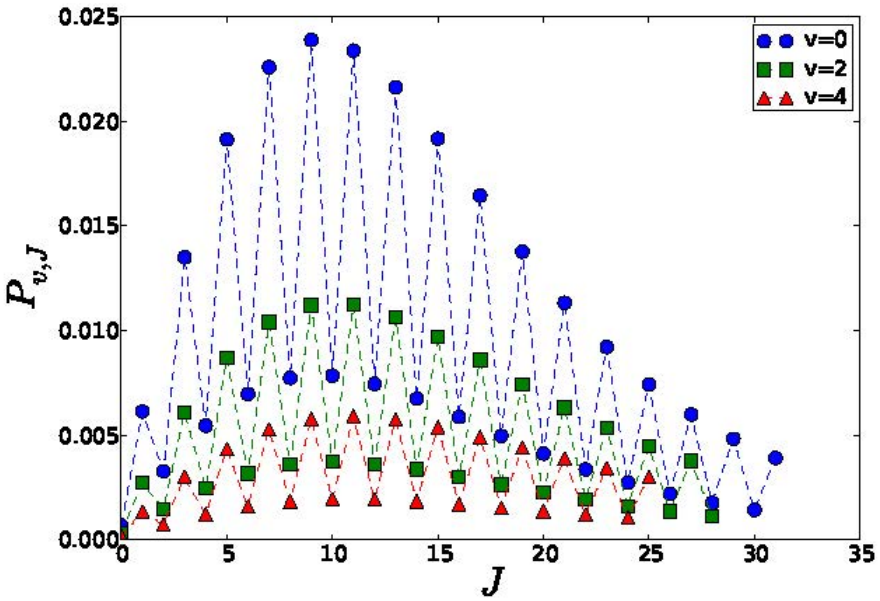
In search for the
Chameleon scenario

$\phi_{WD}=(GM/Rc^2)=10^4\phi_{Earth}$


GD133 spectrum: H2 model, T=11800 K
H2 transitions, z=0.0001820
G29-38 spectrum: H2 model, T=14500 K
H2 transitions, z=0.0001360
CI
CII ISM
CII
SiII
Normalized Flux

Contributions of many lines in the B-X Lyman system





High temperatures
High v populated
Franck-Condon factors

$$P_{wJ}(T) = \frac{g_I(J)(2J+1)\exp\left(\frac{-E_{wJ}}{kT}\right)}{\sum_{v=0}^{v_{max}}\sum_{J=0}^{J_{max}(v)} g_I(J)(2J+1)\exp\left(\frac{-E_{wJ}}{kT}\right)}$$

Dependence of $\Delta\mu/\mu$ on gravitational field

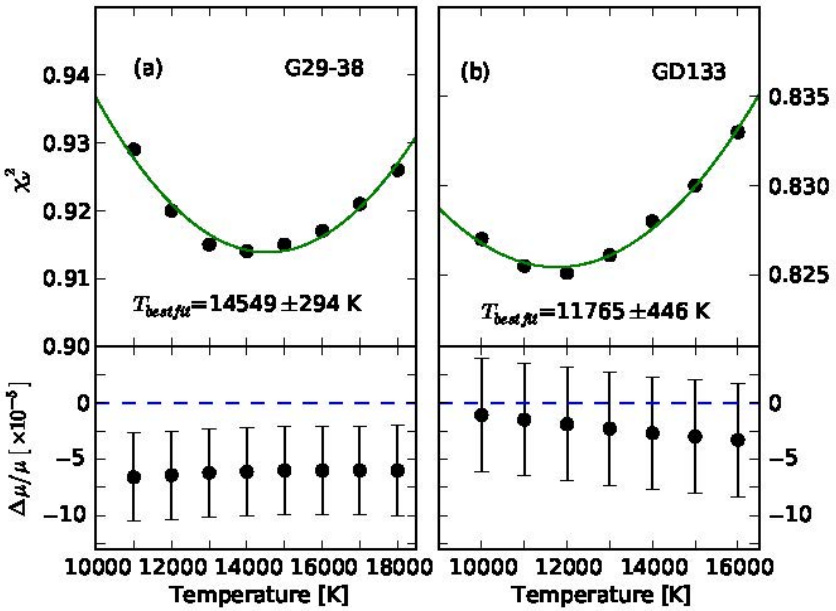
Invoke partition function:

$$P_{vJ}(T) = \frac{g_I(J)(2J+1)\exp\left(\frac{-E_{vJ}}{kT}\right)}{\sum_{v=0}^{v_{max}}\sum_{J=0}^{J_{max}(v)} g_I(J)(2J+1)\exp\left(\frac{-E_{vJ}}{kT}\right)}$$

Invoke intensities (1500 lines):

$$I_i = N_{col} f_{v'v''J'J''} P_{v''J''}(T)$$

Fit T and $\Delta\mu/\mu$

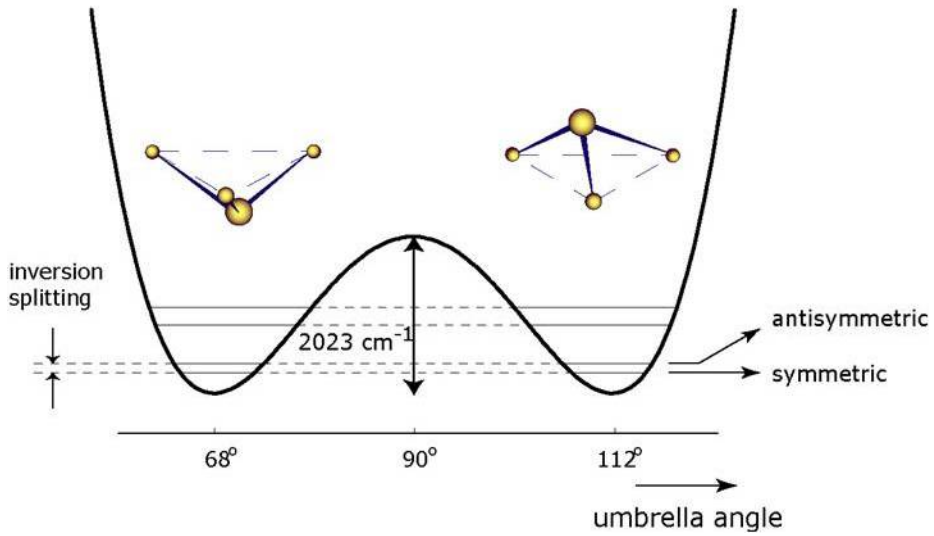


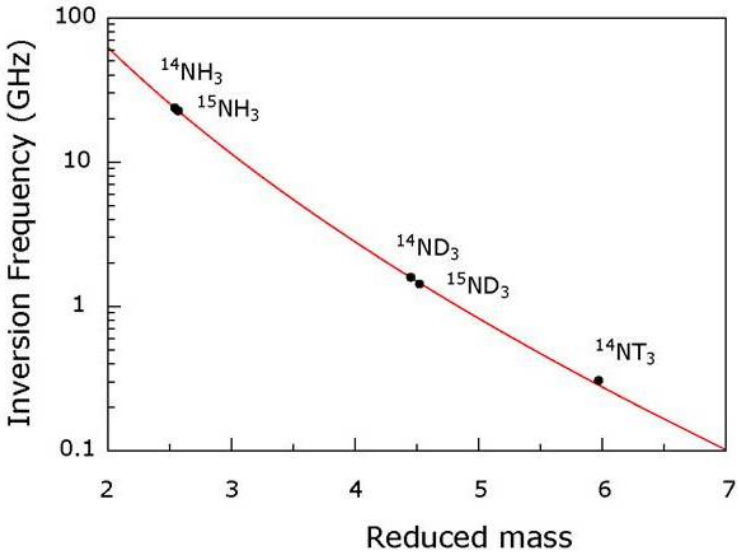
GD133: $\Delta\mu/\mu$ = (-2.7 +/- 4.7) x 10^{-5}

GD29-38: $\Delta\mu/\mu$ = (-5.9 +/-3.8) x 10^{-5}

Outlook: More sensitive molecules

Quantum tunneling





K = -4.2

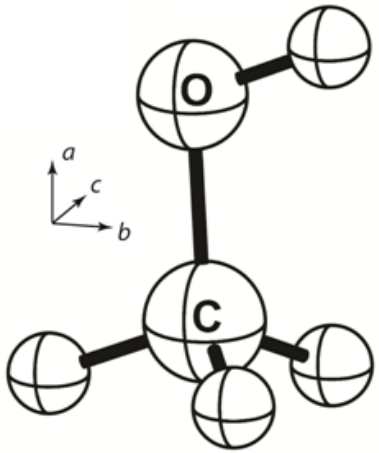
Outlook: More sensitive molecules

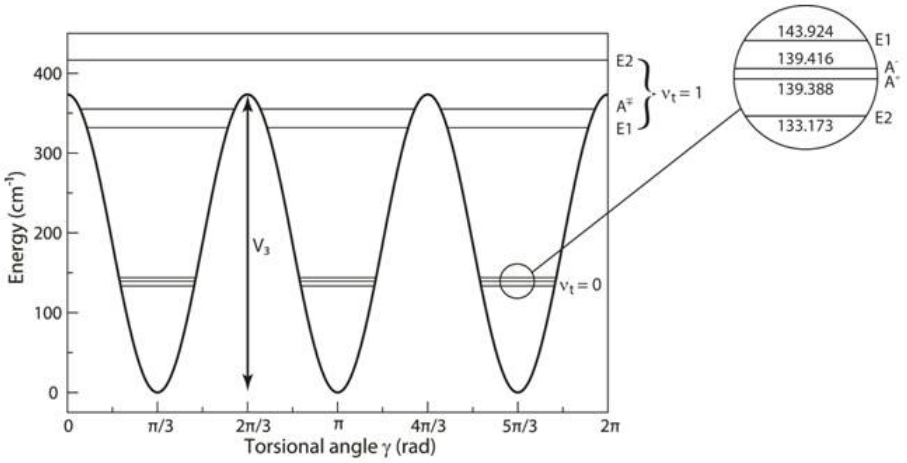
Quantum tunneling: hindered rotation

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

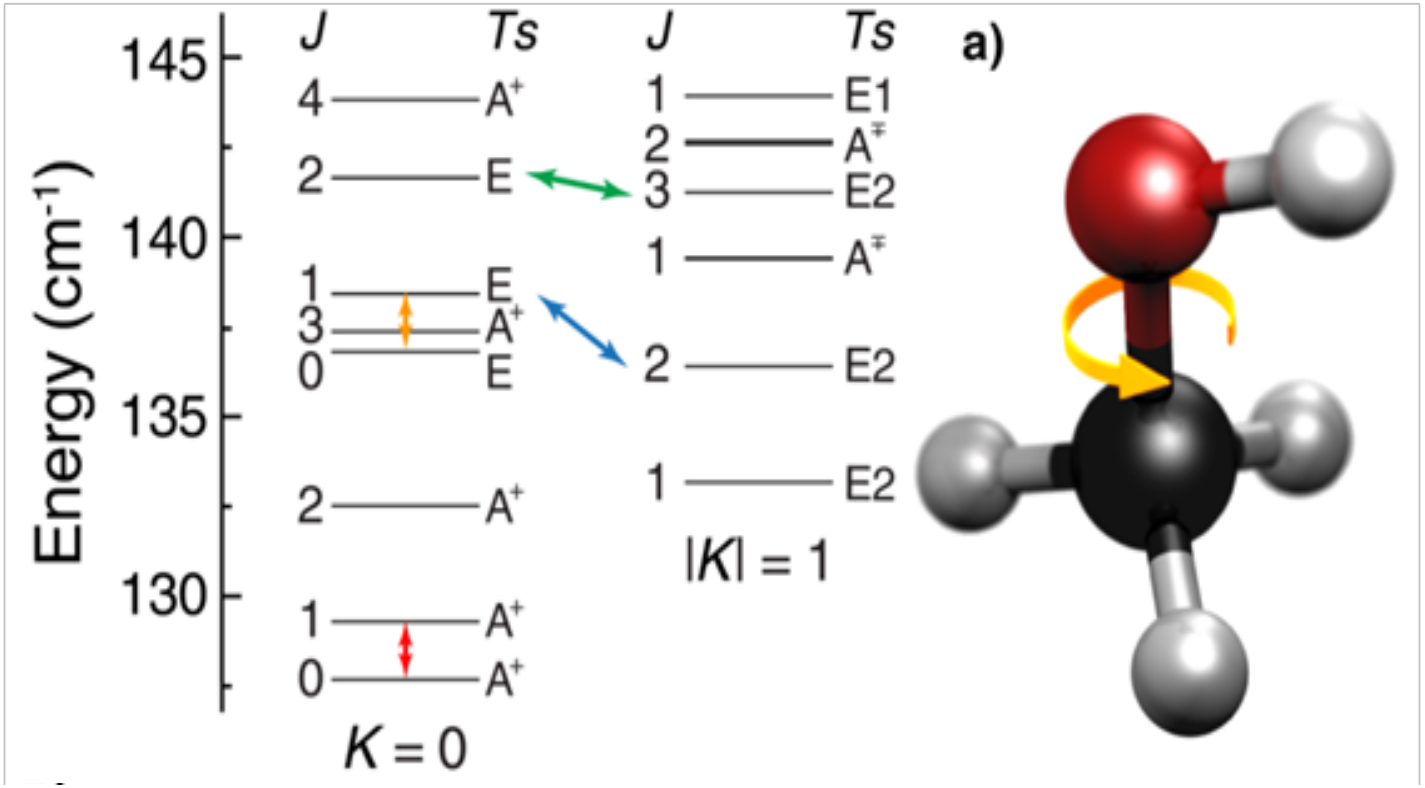
Paul Jansen,[1] Li-Hong Xu,[2] Isabelle Kleiner,[3] Wim Ubachs,[1] and Hendrick L. Bethlem[1]





Calculations ⟶ Extreme shifters

Extreme shifters; towards radio astronomy



48372.4558 MHz; K=-1

48376.892 MHz; K=-1

12178.597 MHz; K=-33

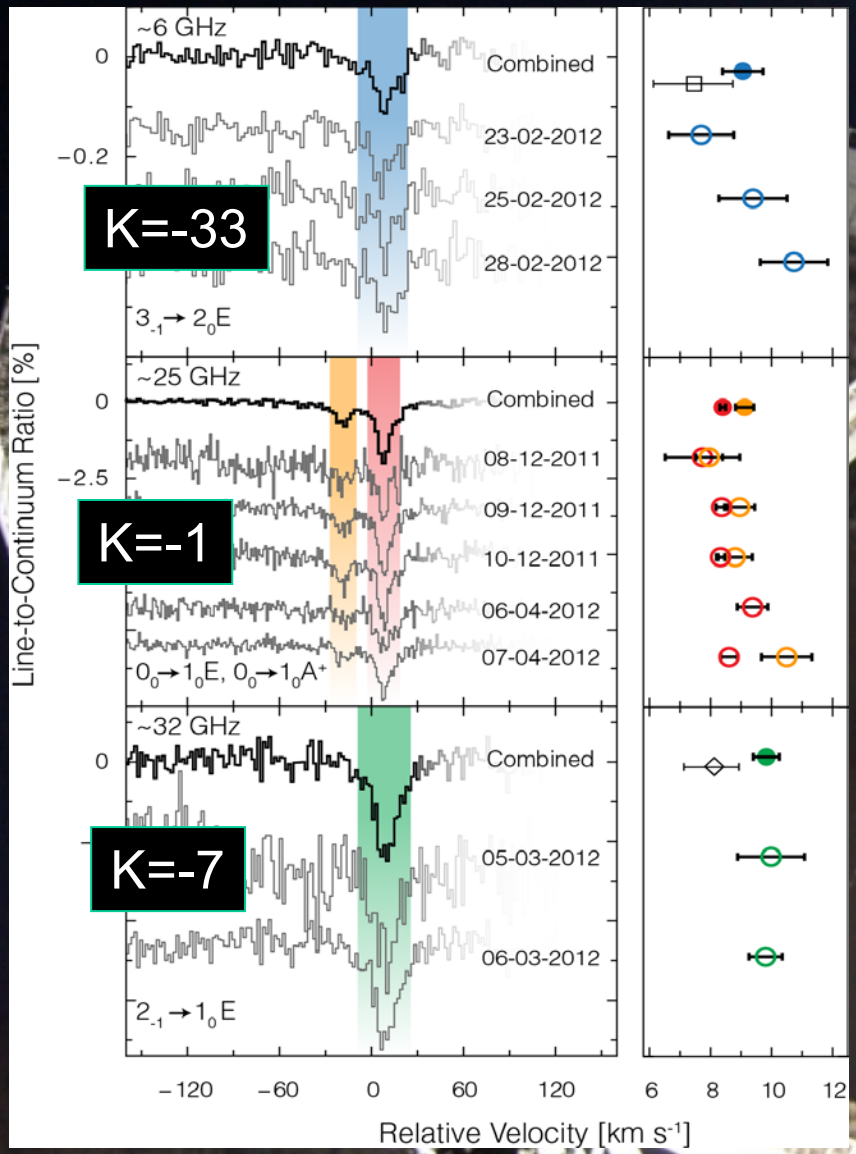
60531.1489 MHz; K=-7

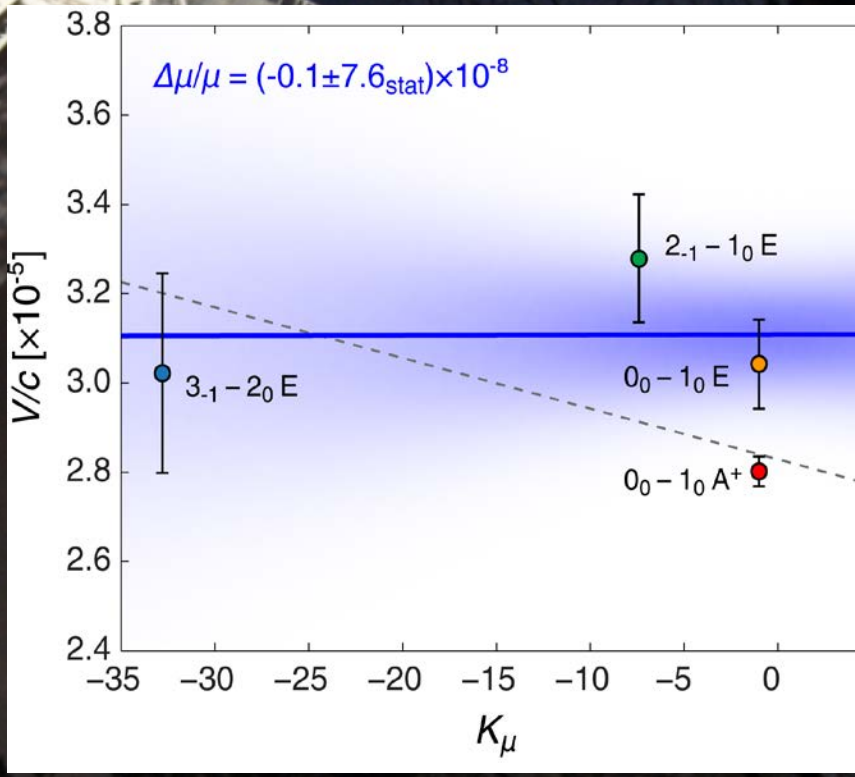

Effelsberg Radio Telescope

Effelsberg Radio Telescope

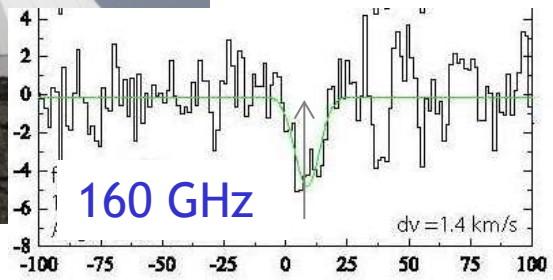
PKS-1[illegible]0-211

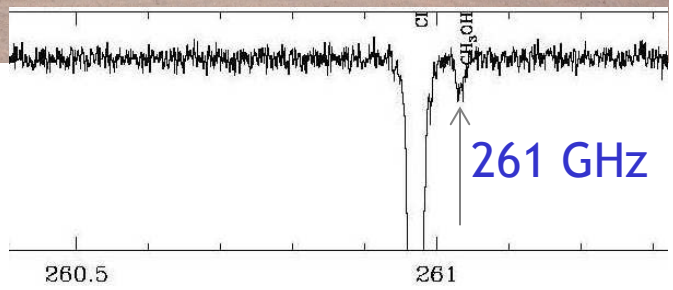
at z=0.88582
(7 Gyrs look-back)





Robust Constraint on a Drifting Proton-to-Electron Mass Ratio at $z = 0.89$ from Methanol Observation at Three Radio Telescopes





Lectures ICTP Winter School on Optics 2016

Precision Spectroscopy of Molecular Hydrogen
and Physics Beyond the Standard Model

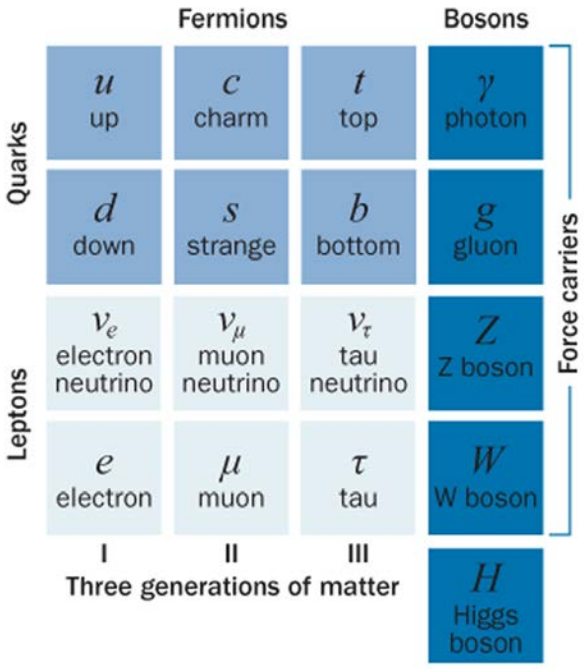
Wim Ubachs
LaserLaB, Vrije Universiteit Amsterdam

Part 3

3) New forces and dimensions from precision studies of H_2

The Standard Model of Physics

What do we know ?



What do we not know ?

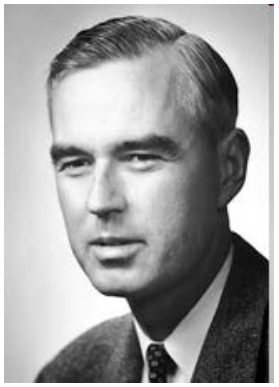
- Dark Matter
- Dark Energy
- How does Gravity fit to SM ?
- Why is Gravity so weak ?
- Constants are constant ?

Are there only 3+1 dimensions ?
Are there only 4 forces ?

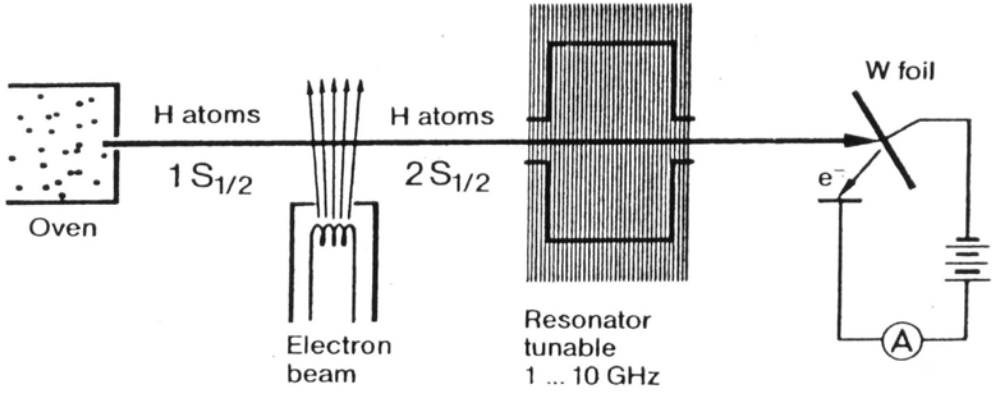
In atomic/molecular systems:
- Gravity can be ignored
- QCD can be ignored (except nuclear spin)
- Weak force can be ignored (in light systems)

Test of QED = Test of Standard model

Historical Note: Lamb shift



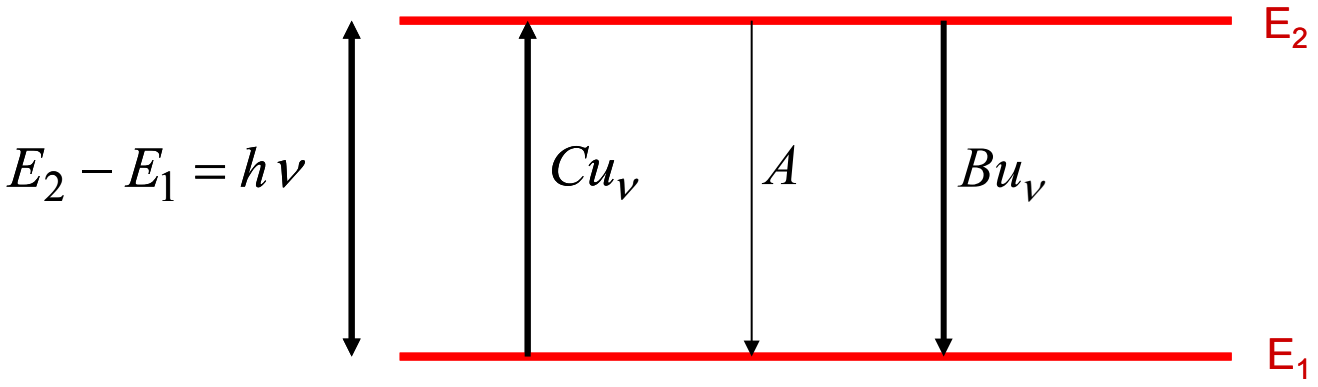
Willis E Lamb



Measurement of the tiny $2S_{1/2} - 2P_{1/2}$ splitting in H-atom

Breakdown of the Dirac theory of the electron
The advent of Quantum Electro Dynamics

Precision measurements on quantum levels:
on weak and strong lines



Einstein coefficients

$$C = B$$

$$\frac{A}{B} = \frac{8\pi h\nu^3}{c^3}$$

Dipole strength

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

Lifetime

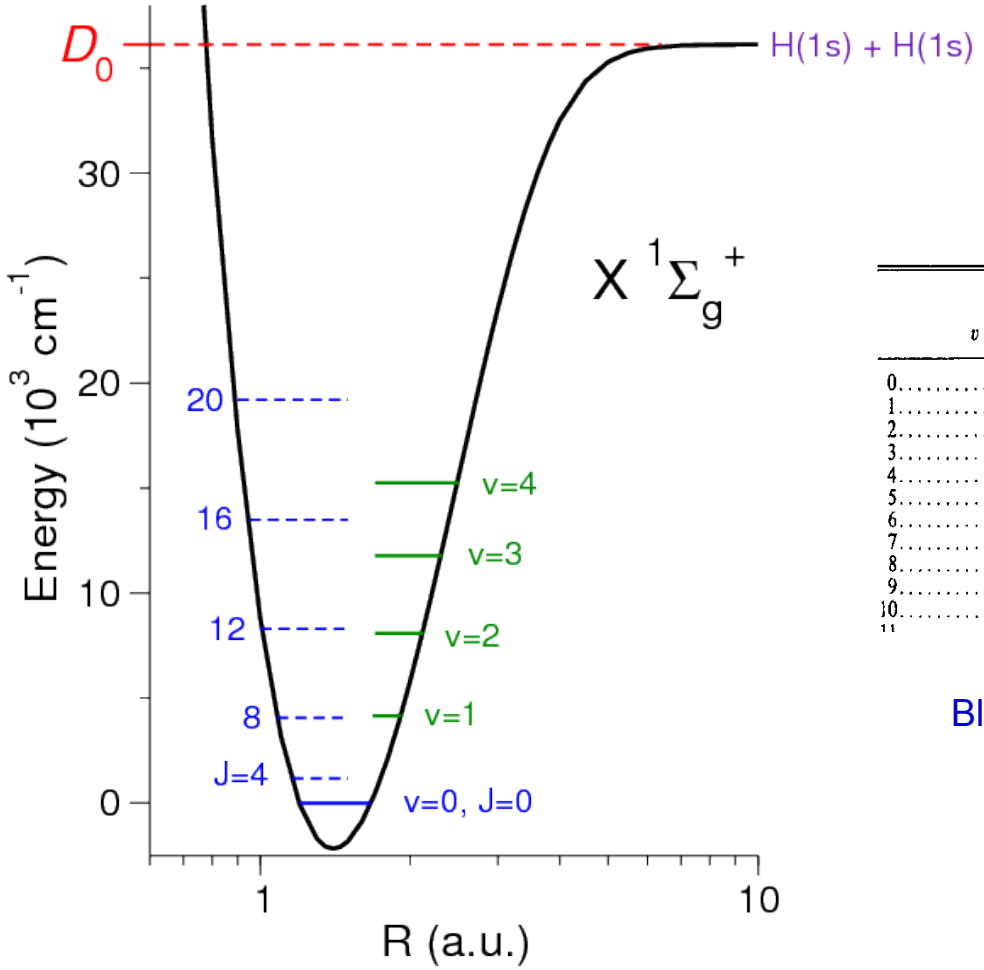
$$\tau = \frac{1}{A}$$

Heisenberg uncertainty

$$\Gamma = \frac{1}{2\pi\tau}$$

Strong lines → broadened
Weak lines → narrow

QED in the H_2 ground state



1000 cm^{-1} = 0.1239 eV

Long-lived quantum states
H_2 has no dipole moment

TABLE 1

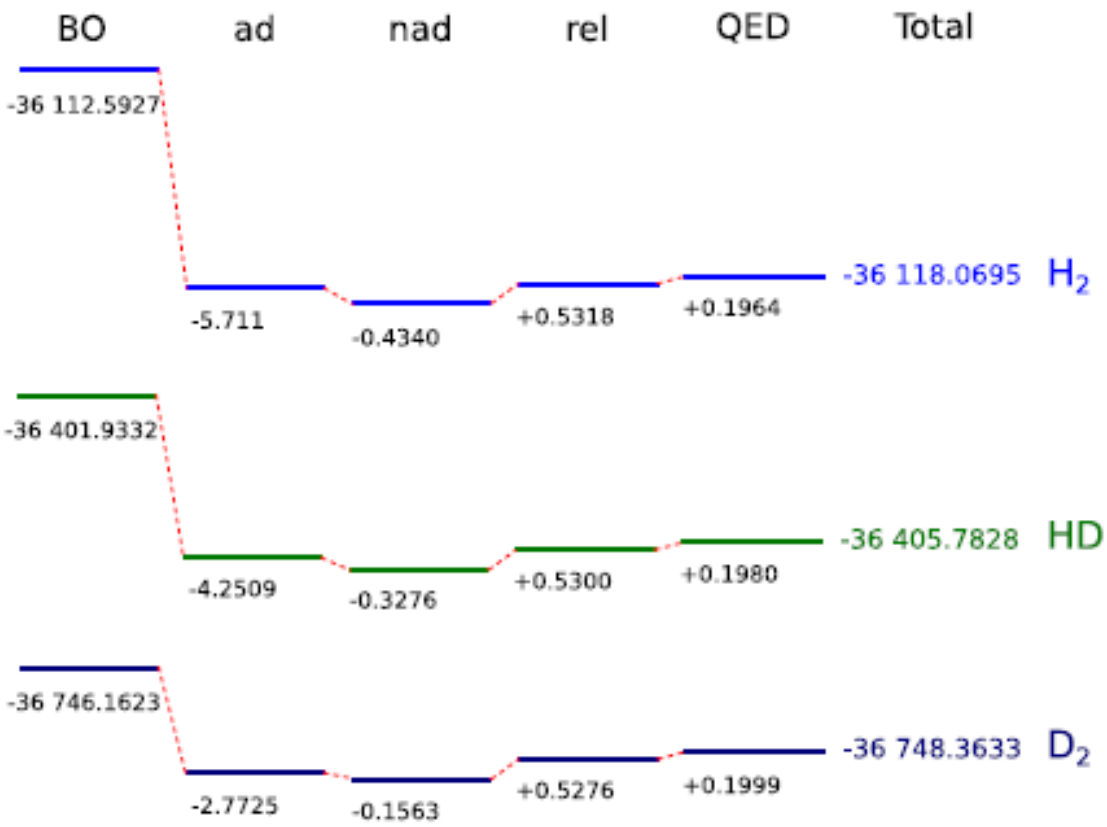
LIFETIMES $\tau(vJ)$ OF THE ROTATION-VIBRATIONAL LEVELS OF H_2 IN UNITS OF 10^6 SECONDS

	J								
v	0	1	2	3	4	5	6	7	8
0	...	...	3.39(4)*	2.10(3)	3.63(2)	1.02(2)	37.9	17.0	8.75
1	1.17	1.17	1.18	1.20	1.22	1.26	1.31	1.36	1.40
2	0.612	0.612	0.614	0.618	0.628	0.644	0.668	0.698	0.735
3	0.422	0.422	0.426	0.422	0.425	0.433	0.446	0.464	0.488
4	0.328	0.327	0.325	0.324	0.326	0.329	0.337	0.349	0.365
5	0.270	0.269	0.268	0.266	0.266	0.268	0.273	0.282	0.294
6	0.234	0.233	0.231	0.230	0.229	0.231	0.234	0.241	0.251
7	0.211	0.210	0.209	0.207	0.206	0.207	0.211	0.216	0.225
8	0.198	0.197	0.196	0.194	0.194	0.195	0.198	0.204	0.213
9	0.194	0.193	0.192	0.191	0.191	0.192	0.196	0.203	0.213
10	0.199	0.199	0.198	0.197	0.198	0.200	0.206	0.214	0.227
11	0.217	0.217	0.217	0.217	0.219	0.224	0.233	0.246	0.266

Black and Dalgarno, Astroph. J. 203 (1976) 132

Possibility for precision spectroscopy
- Very weak transitions
- Use excited states ?

Decomposition of dissociation energy in H_2



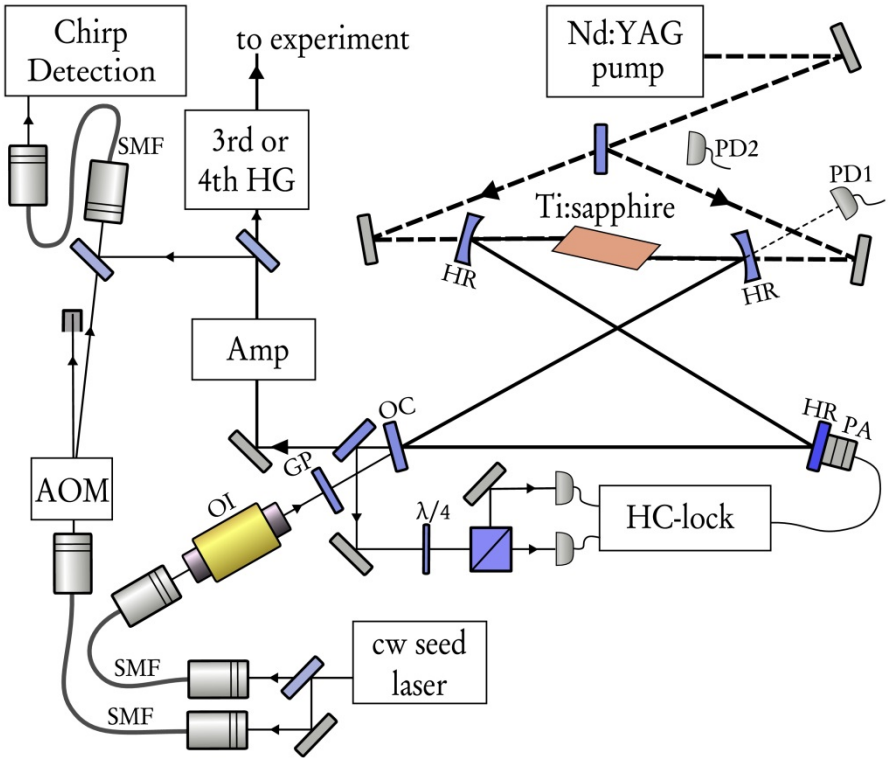
For v=0, J=0

Ab initio theory:

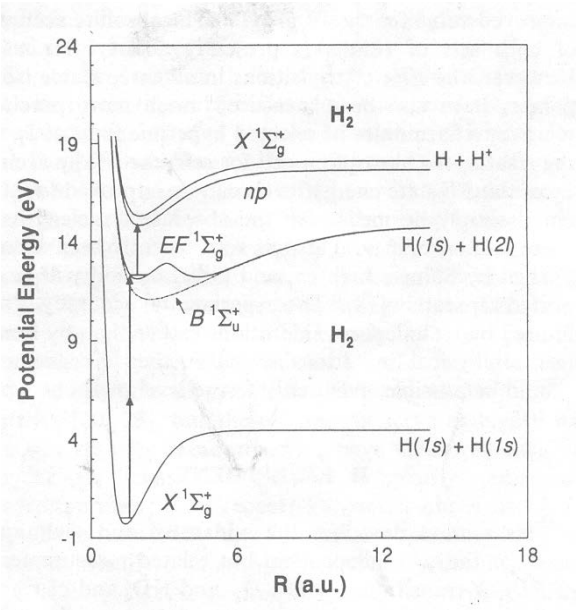
K. Pachucki et al., *JCTC* **5**, 3039 (2009)

and many papers

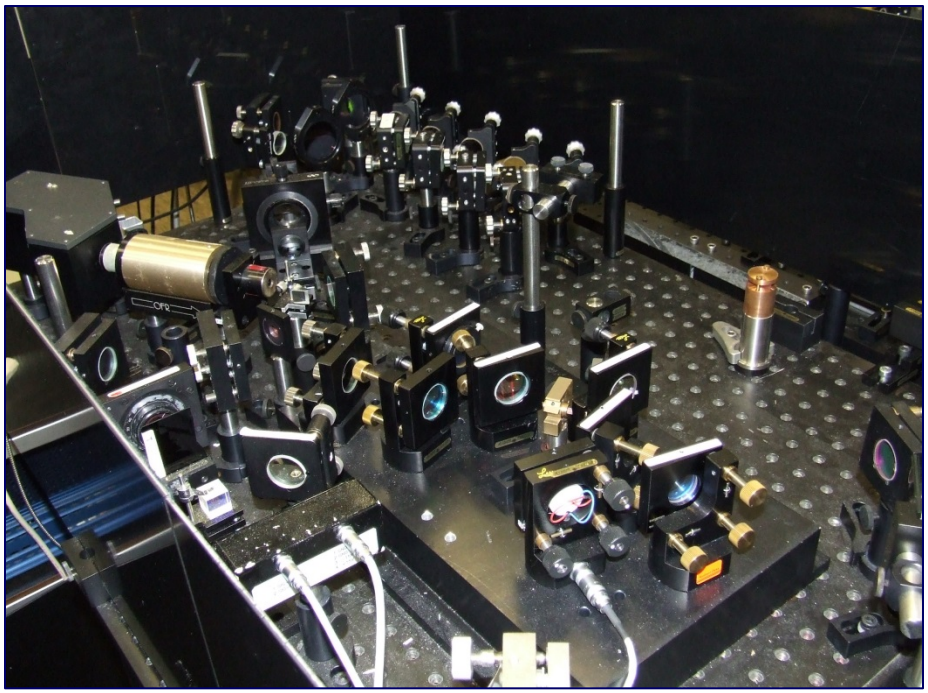
Frequency metrology of the EF-X two photon transition in H_2



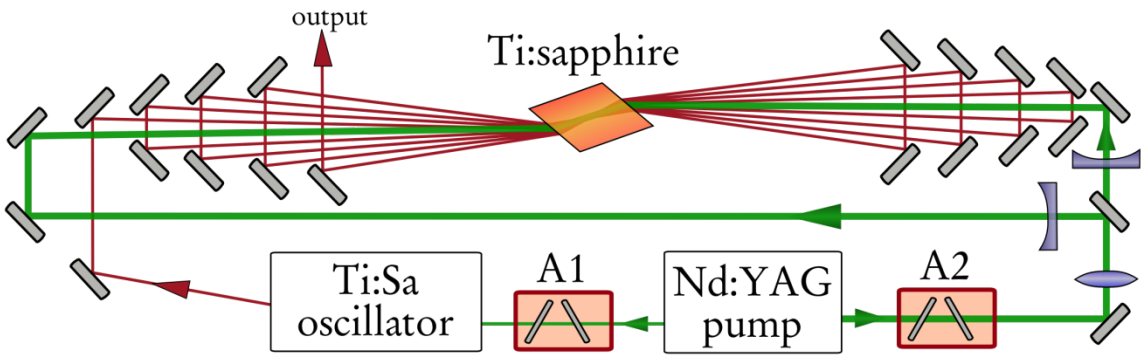
Fourier-transform limited pulses, 20-40 ns

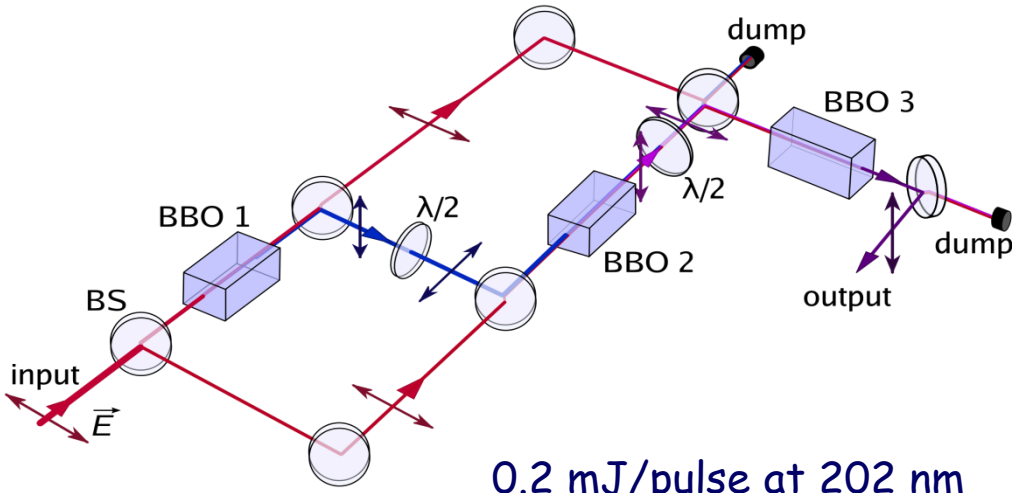


EF, v=0, J=0
τ = 150 ns

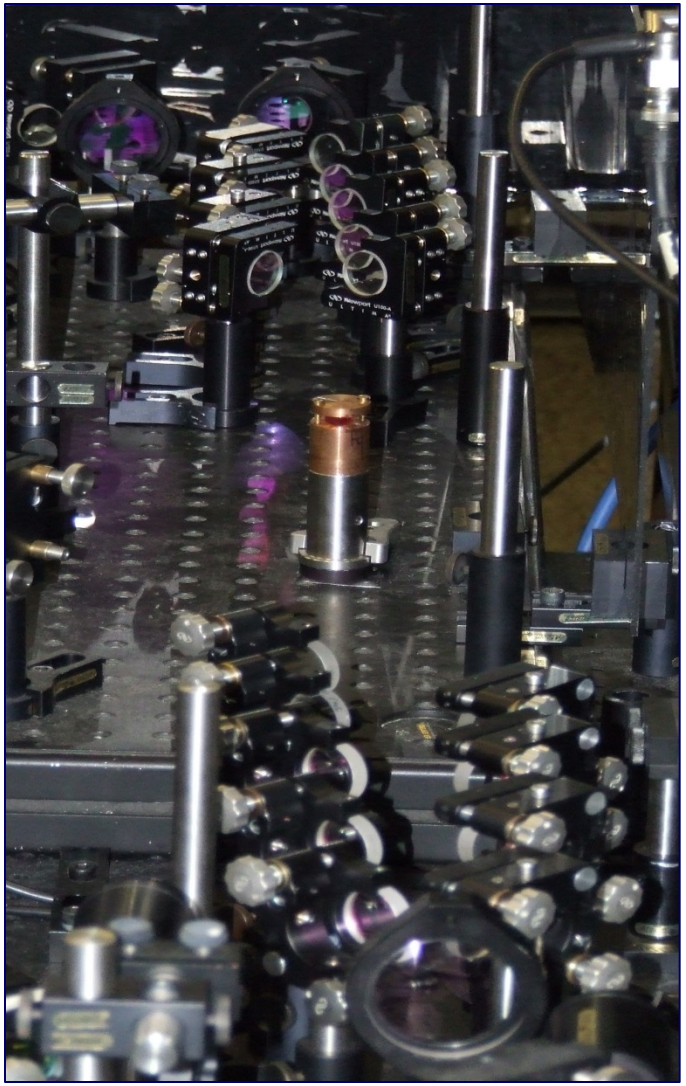


Amplifier and conversion to deep-UV



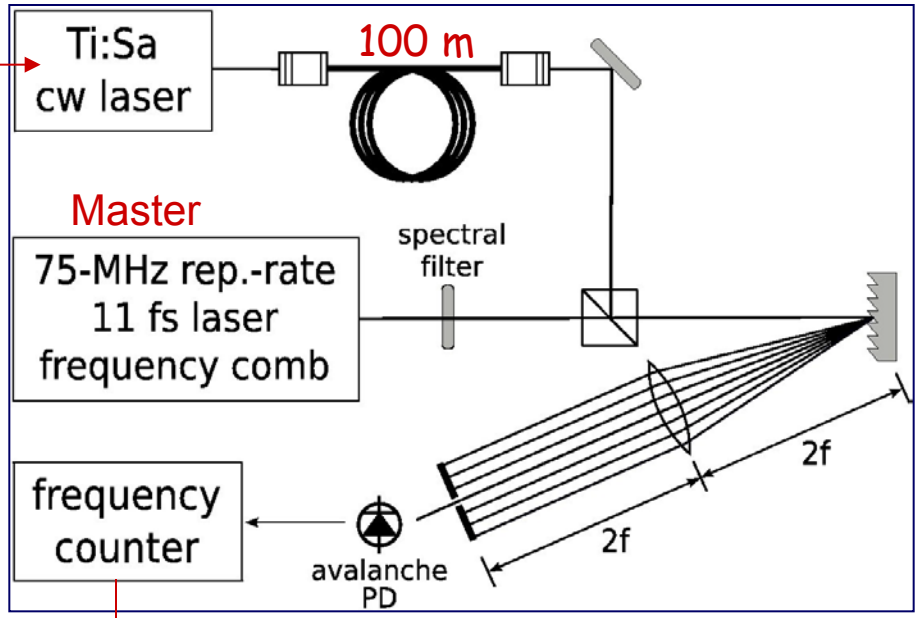


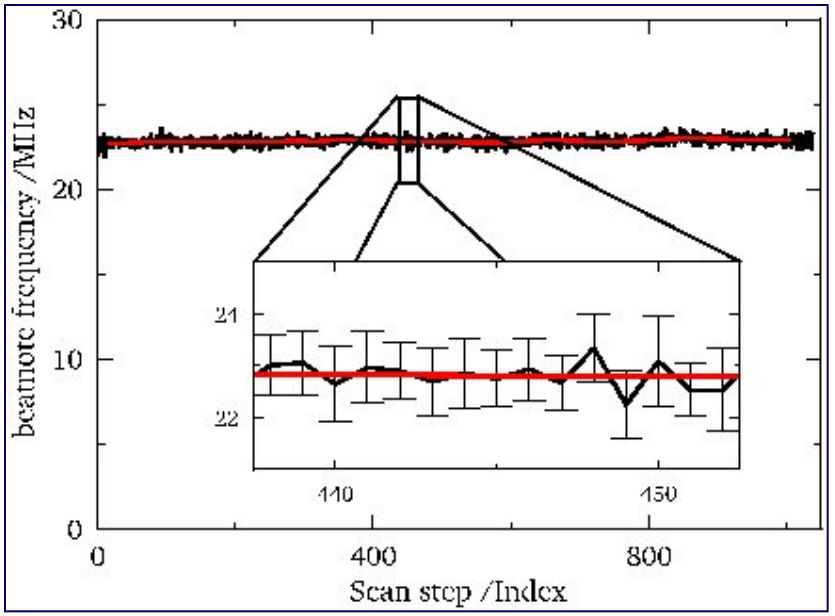
0.2 mJ/pulse at 202 nm



Frequency measurement via Frequency-comb laser

Measure f_{cw} via beat-note comb, via RF filter





Fix at 22 MHz

S. Hannemann et al. Phys. Rev. A74, 062514 (2006)

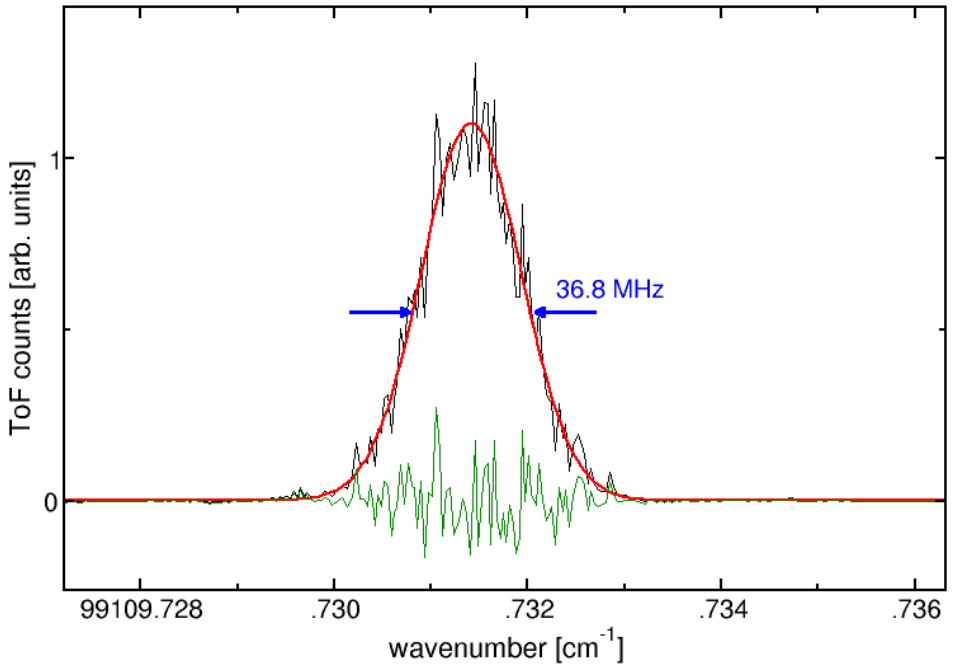
Result

PHYSICAL REVIEW A 74, 062514 (2006)

Frequency metrology on the $EF\ ^1\Sigma_g^+ \leftarrow X\ ^1\Sigma_g^+(0,0)$ transition in H_2, HD, and D_2

S. Hannemann, E. J. Salumbides, S. Witte, R. T. Zinkstok, E. -J. van Duijn, K. S. E. Eikema, and W. Ubachs
Laser Centre, Department of Physics and Astronomy, Vrije Universiteit, De Boelelaan 1081, 1081 HV Amsterdam, The Netherlands
(Received 11 October 2006; published 28 December 2006)

H_2 EF-X (0,0) Q(1) line

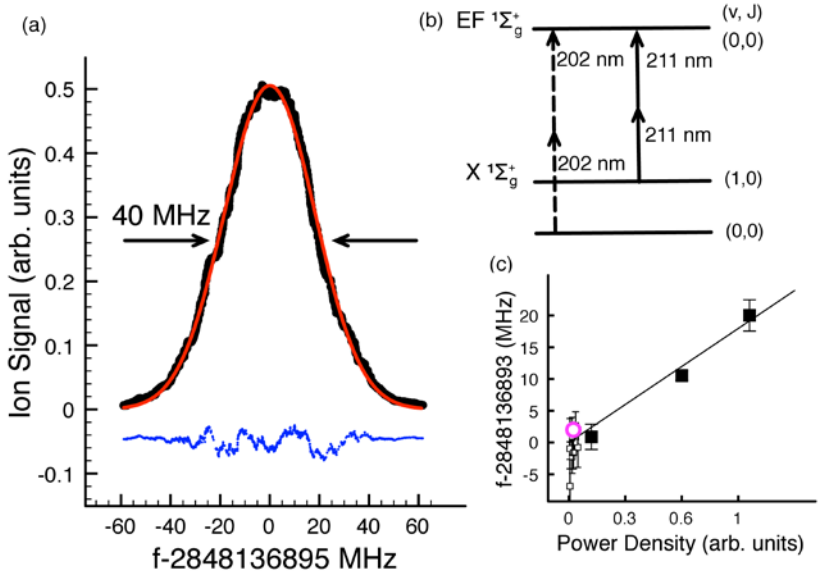


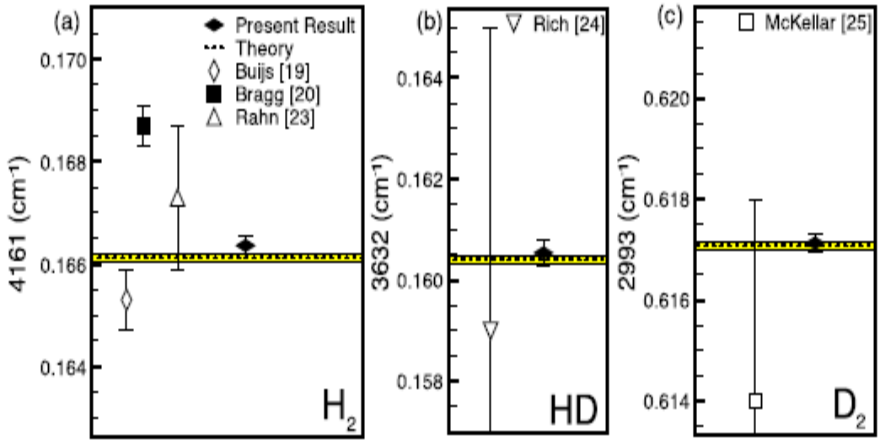
Transition Energies		
H_2	Q0	99164.78691(11)
	Q1	99109.73139(18)
	Q2	99000.18301(11)
HD	Q0	99301.34662(20)
	Q1	99259.91793(20)
D_2	Q0	99461.44908(11)
	Q1	99433.71638(11)
	Q2	99378.39352(11)

$\Delta\lambda/\lambda = 1 \times 10^{-9}$

Fundamental vibration in H_2

- High Precision measurements on rotation less X $^1\Sigma^+_g$-EF $^1\Sigma^+_g$ (0,1) band
- Bypassing the *direct* quadrupole measurement
- Accuracy of **2×10^{-4} cm^{-1}**
- Good agreement with *ab initio* provides a stringent test of QED in molecules



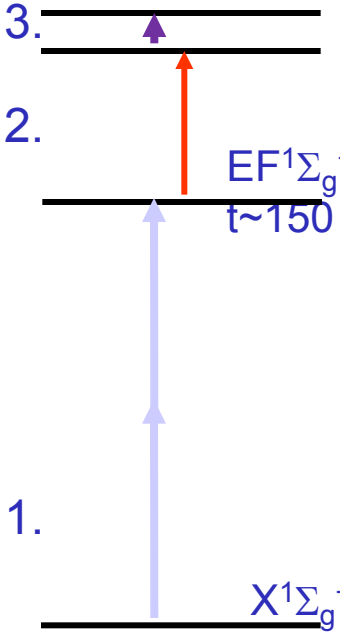


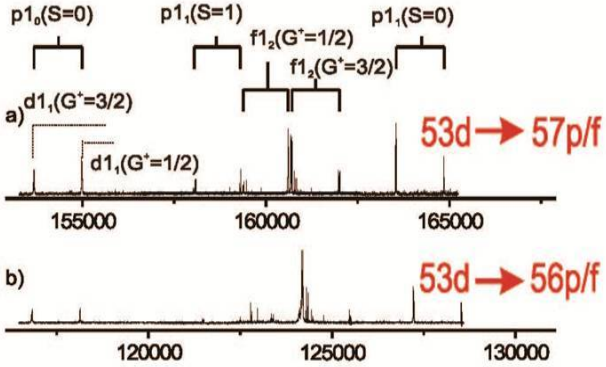
1σ uncertainty with *ab initio* calculations

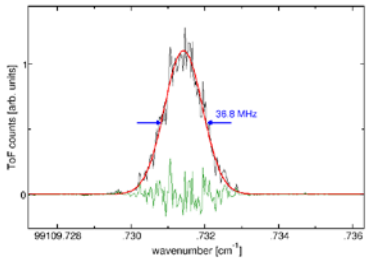
Dickenson *et.al*, Phys. Rev. Lett., 110, 193601 (2013)

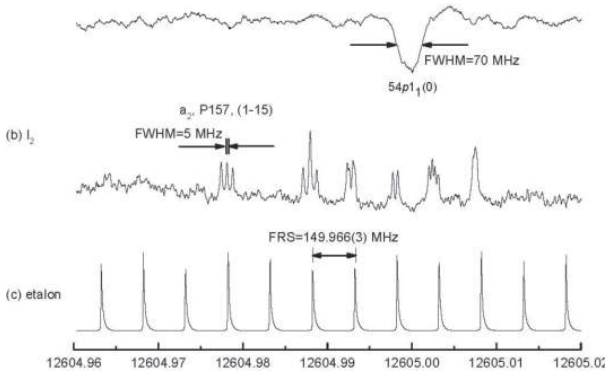
Measurement of IP in H_2 : 3 step approach

H_2^+ : $X^2\Sigma_g^+$,
$v^+=0$, $N^+=0,1$





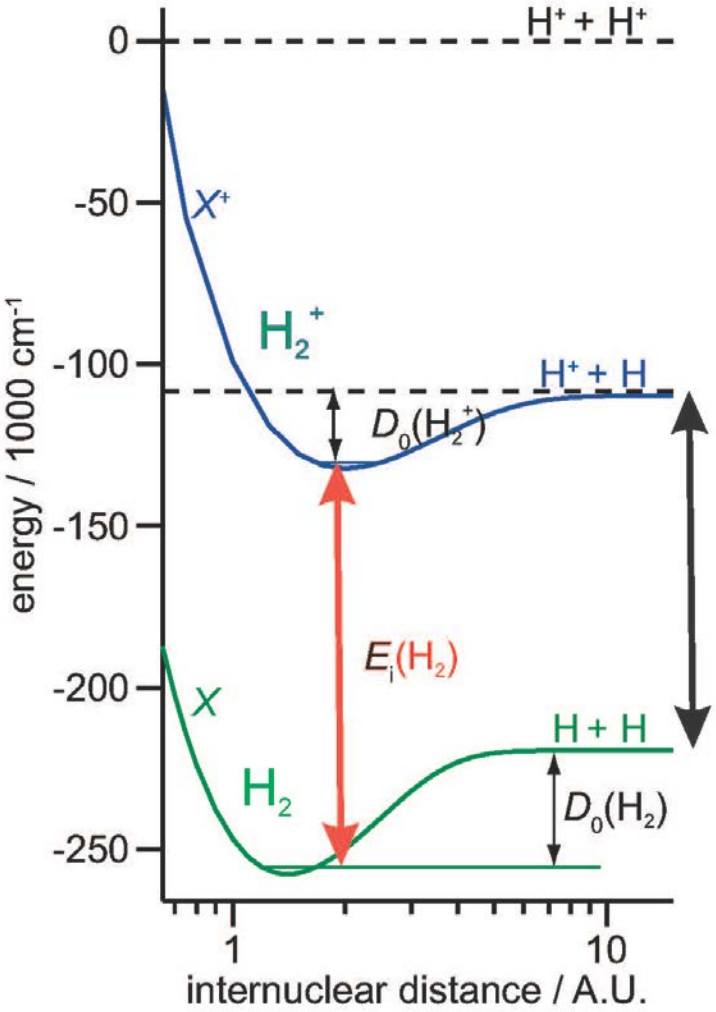




E_i (ortho) = 124 357.237 97 (36) cm^{-1}

E_i (para) = 124 417.491 13 (37) cm^{-1}

Benchmark: Dissociation energy H_2



$$D_o(H_2) = E_{IP}(H_2) + D_o(H_2^+) - E_{IP}(H)$$

$$D_o(H_2^+) = 21379.350232(50)\ cm^{-1}$$

$$E_{IP}(H) = 109678.7717426(10)\ cm^{-1}$$

$$E_{IP}(H_2) \rightarrow D_o(H_2)$$

D_0: Comparison Theory/Experiment

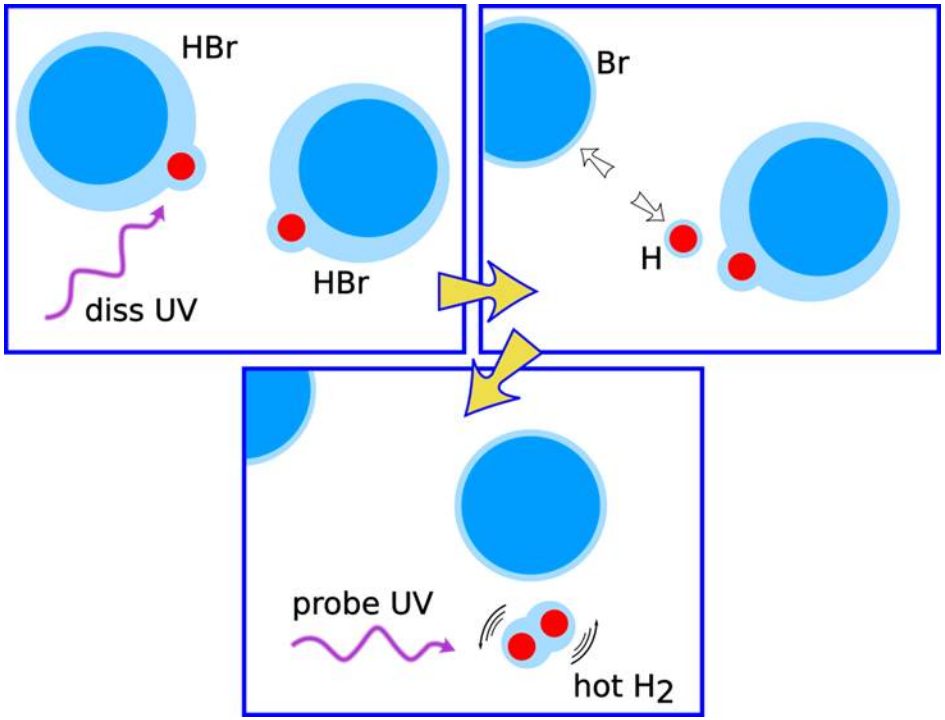
Theory:
Pachucki et al.

$D_0(H_2)$:	Experiment [1]	36118.0696(4) cm^{-1}
	Theory [2]:	
	Born–Oppenheimer	36112.5927(1) cm^{-1}
	adiabatic	+ 5.7711(1) cm^{-1}
	nonadiabatic	+ 0.4339(2) cm^{-1}
	total α^0	36118.7978(2) cm^{-1}
	α^2 all relativistic	– 0.5319(5) cm^{-1}
	α^3 all QED	– 0.1948(3) cm^{-1}
	α^4 one-loop term	– 0.0016(8) cm^{-1}
	Total theory	36118.0695(10) cm^{-1}
$D_0(D_2)$:	Total theory [2]	36748.3633(9) cm^{-1}
	Experiment [4]	36748.3629(7) cm^{-1}

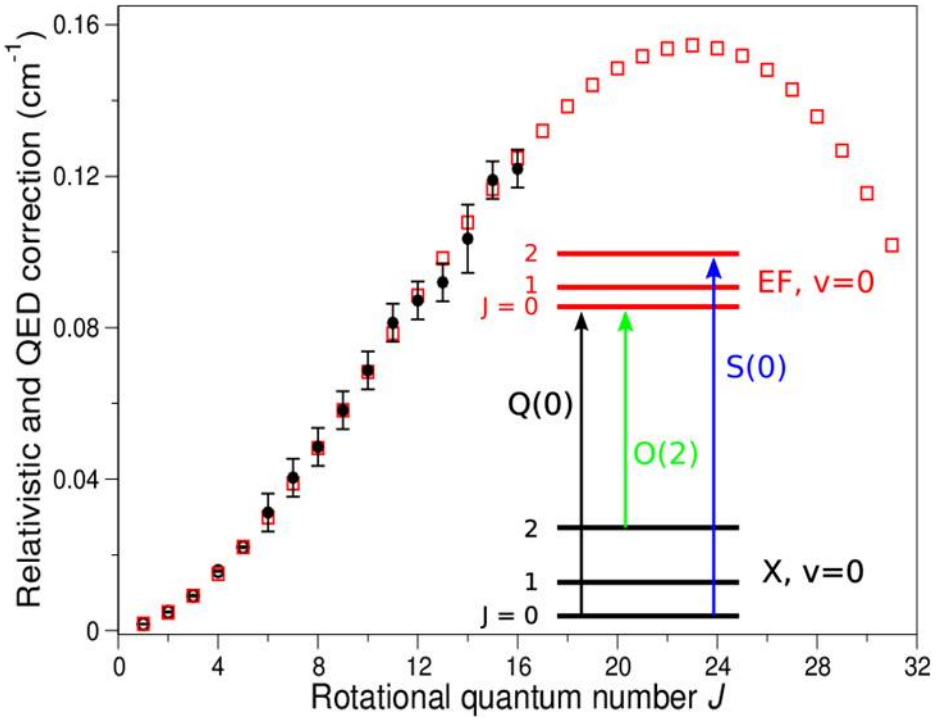
QED

Rotational effects on QED: hot hydrogen

Photolysis chemical production of hot H_2



Two-photon spectroscopy/ compare QED



J_{max} (v=0) = 8

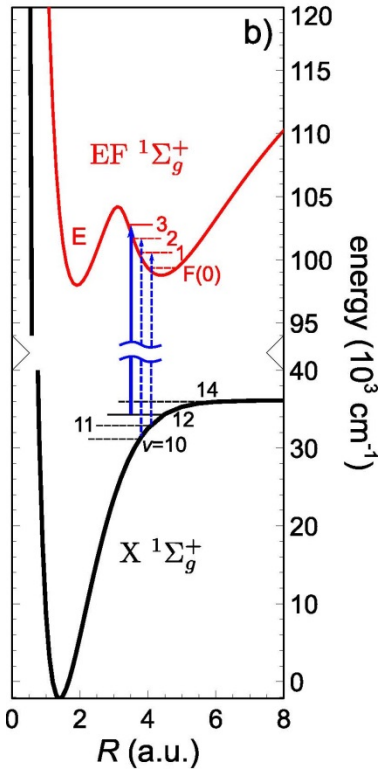
T_{equiv} = 12,000 K

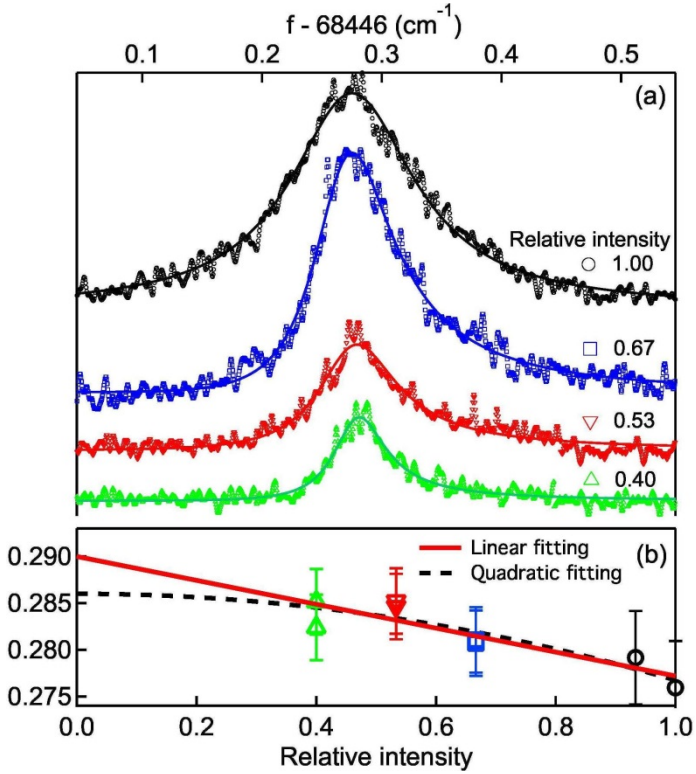
Phys. Rev. Lett. 107, 043005 (2011)

Precision study of H_2 $X^1\Sigma_g^+$ v=12

Production of H_2, v=12
Photolysis of H_2S
Steadman & Baer (1989)

Now;
Three independent lasers





J''	E_{exp}	E_{the}	$\Delta E_{exp-the}$
0	34 302.1823 (35)	34 302.1741 (47)	0.008 (6)
1	34 343.8531 (35)	34 343.8483 (46)	0.005 (6)
2	34 426.2216 (35)	34 426.2179 (46)	0.004 (6)
3	34 547.3362 (35)	34 547.3332 (45)	0.003 (6)

JCP Comm 142 (2015) 081102

Experiment – QED Calculation comparisons

Species	Splitting	δE_{exp}	Ref.	δE_{calc}	δE	ΔE	
H_2	$v = 0, J = 6 - 12$	150[c]	[56]	12	150[c]	20	MHz
	$v = 0, J = 13 - 16$	300[c]	[56]	27	300[c]	90	
	$v = 0 \rightarrow 1$	4.5[a]	[54]	2.7	5	7	
	$v = 0 \rightarrow 2$	30	[57]	50	60	12	
	$v = 0 \rightarrow 3$	1.3	[58]	75	75	10	
	$v = 0 \rightarrow 12$	105	[59]	140	170	150[b]	
	D_0	12	[44]	30	3	36	
HD	$v = 0 \rightarrow 1$	7[a]	[54]	2.4	8	4	
	D_0	11	[49]	30	27	32	
D_2	$v = 0 \rightarrow 1$	4.5[a]	[54]	2.1	5	−0.6	
	$v = 0 \rightarrow 2$	30	[60]	12	30	−12	
	D_0	21	[48]	27	30	12	

Various precision experiments: full agreement with QED theory

W. Ubachs *et al.*, J. Mol. Spectrosc. **320**, 1 (2016)

Interpretation: Molecules as a metrology test system

Search for physics beyond the Standard Model
from molecular spectroscopy experiment

$$\Delta E = E_{\text{exp}} - E_{theory}$$

$$\delta E = \sqrt{\delta E_{\text{exp}}^2 + \delta E_{theory}^2}$$

$\Delta E < \delta E$ Test of theory (QED)

$\Delta E > \delta E$ New Physics:

Theory is needed – only for "calculable" systems this is possible
→ Hydrogen has become a calculable system

Discover new physics $\left\langle \Delta V_{new} \right\rangle = \Delta E > \delta E$

Is there a fifth force ?

Assume: Extra *hadron-hadron* interaction
Parametrize (quantum field theory) as:

Yukawa potential (Phenomenological)

$$V_5(r) = N_1 N_2 \left\{ \alpha_5 \frac{\exp(-r/\lambda)}{r} \right\} \hbar c$$

Hideki Yukawa

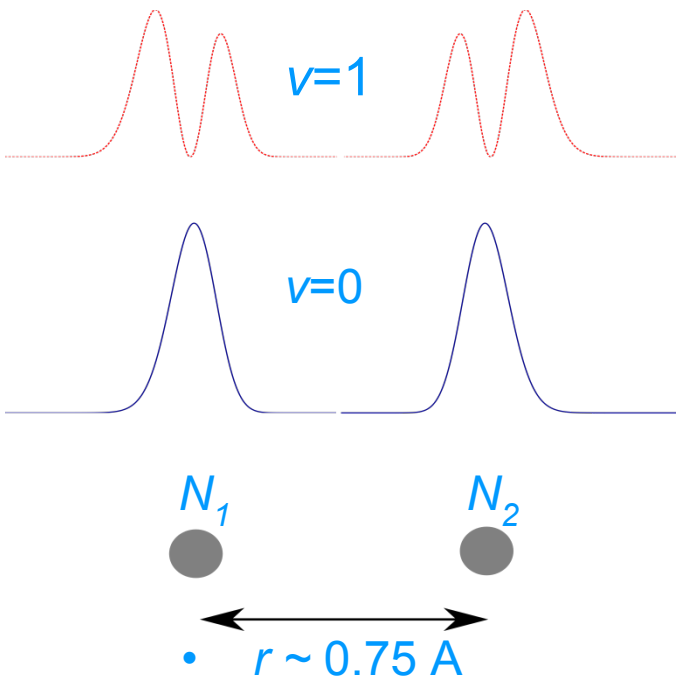
Strength: α_5

Range: $\lambda = \hbar / m_5 c$

Mass of force carrying particle: m_5

Hadron numbers: N_1, N_2

Calculate the expectation value of the energy operator



Level shifts:

$$\langle \Psi_1 | V_5 | \Psi_1 \rangle ; \langle \Psi_0 | V_5 | \Psi_0 \rangle$$

Transition shift:

$$\langle \Psi_1 | V_5 | \Psi_1 \rangle - \langle \Psi_0 | V_5 | \Psi_0 \rangle$$

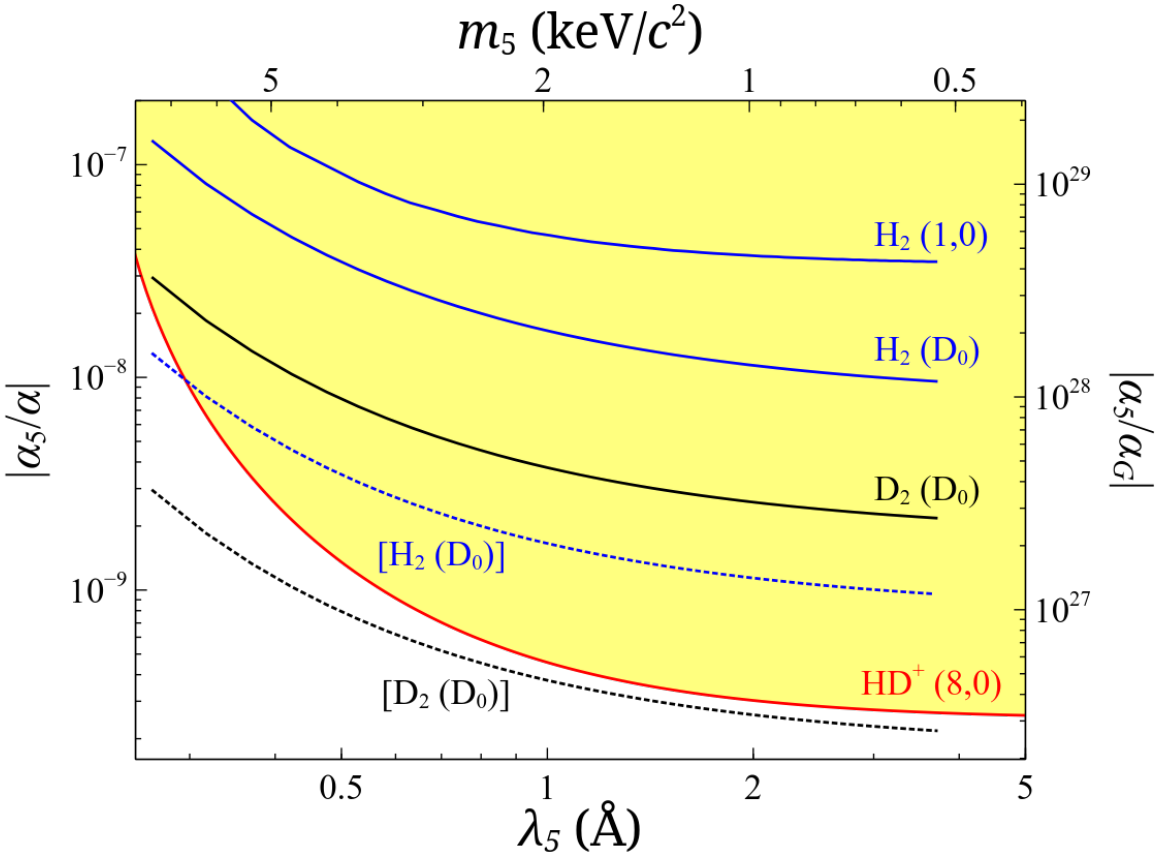
Differential effect larger for very high v's (D_0 limit)

$$\langle \Delta V_{5,\lambda} \rangle = \alpha_5 N_1 N_2 \hbar c \left\{ \left\langle \Psi_{v'J'}(r) \left| \frac{\exp(-r/\lambda)}{r} \right| \Psi_{v'J'}(r) \right\rangle - \left\langle \Psi_{v''J''}(r) \left| \frac{\exp(-r/\lambda)}{r} \right| \Psi_{v''J''}(r) \right\rangle \right\}$$

Calculable from the known wave functions for H_2; parameters α_5 and λ

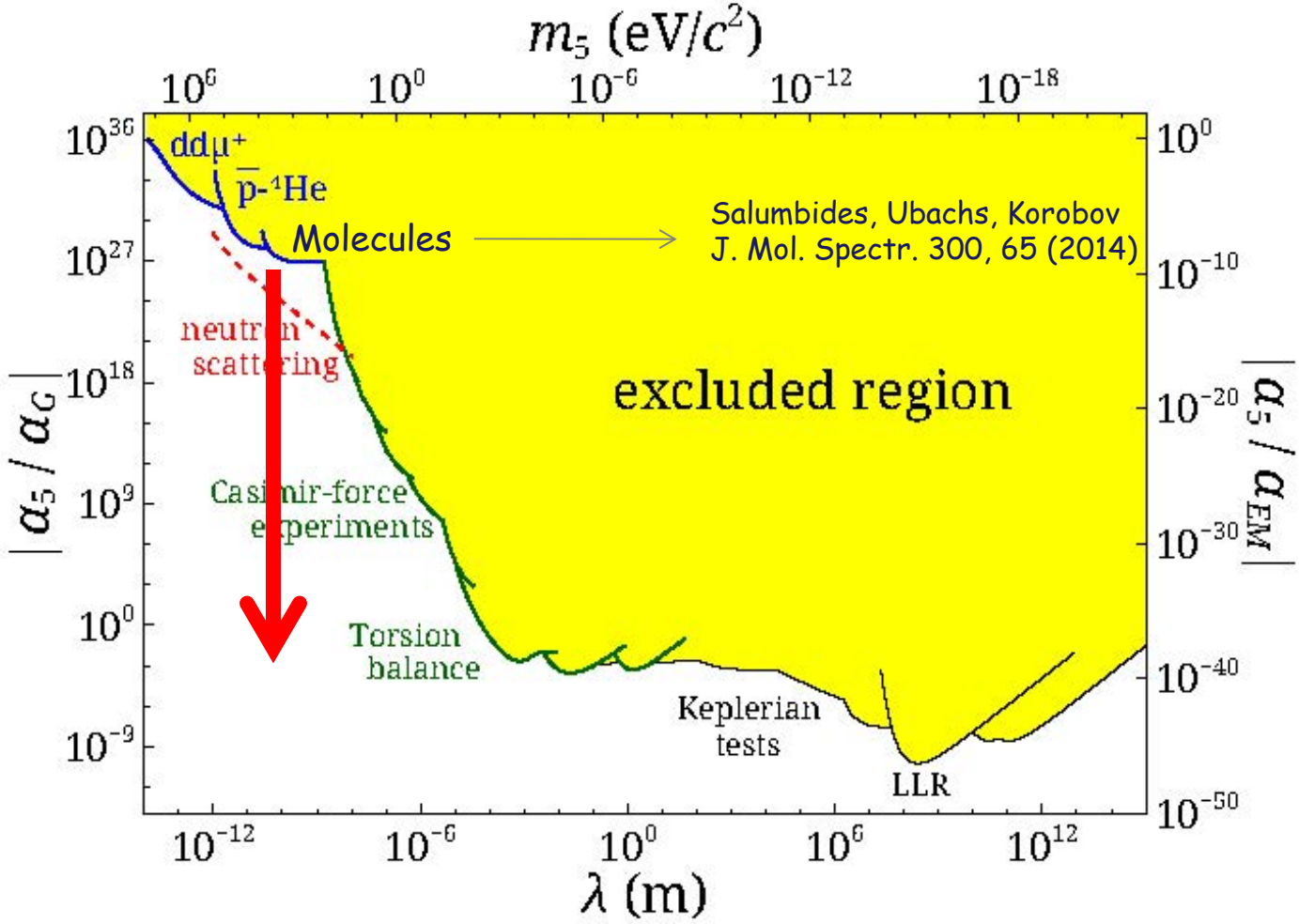
Impose constraints on 5th force from spectroscopy H_2

$$\langle \Delta V_5 \rangle < \delta E \qquad \text{hence} \qquad \alpha_5 < \frac{\delta E}{N_1 N_2 \hbar c \langle \Delta \Psi \rangle}(\lambda)$$



For HD+ see : Nature Comm. 7, 10385 (2016)

Search for 5th forces; the grand picture



Physics of extra spatial dimensions

Immanuel Kant:

Number of dimensions consequence
of Newton's Universal law of gravitation

Immanuel Kant

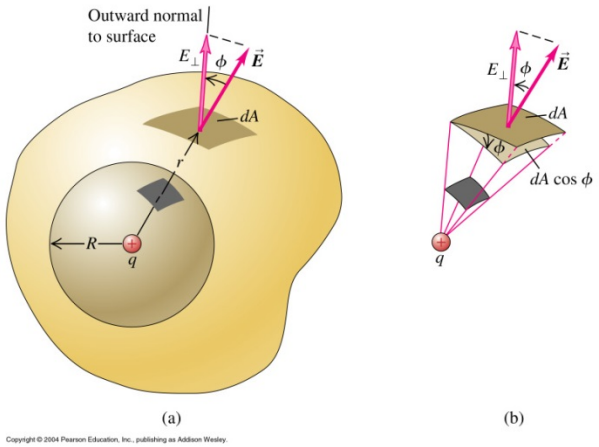
Flux Law:

$$\oint_V \vec{F} \cdot d\vec{A} = kQ_{encl}$$

3-dim: $A_V \propto r^2 \Rightarrow F \propto \frac{1}{r^2}$

N-dim: $A_V \propto r^{N-1} \Rightarrow F \propto \frac{1}{r^{N-1}}$

Gravitational attraction
depends on dimensionality

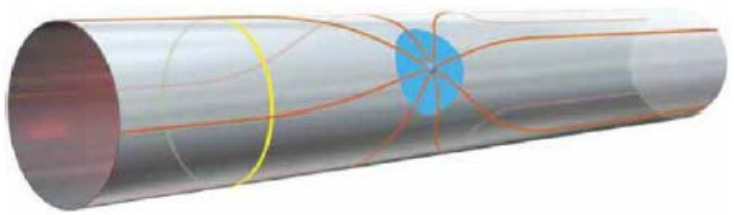


“Compactification”

Theory of consistent EM + Gravity in 5 dimensions (Kaluza)

Extra dimensions are not observed in the macroscopic world
They may be compactified: rolled up (Klein 1926)

Oscar Klein



String theory: “M-Theory” (Witten) is consistent in 11 dimensions

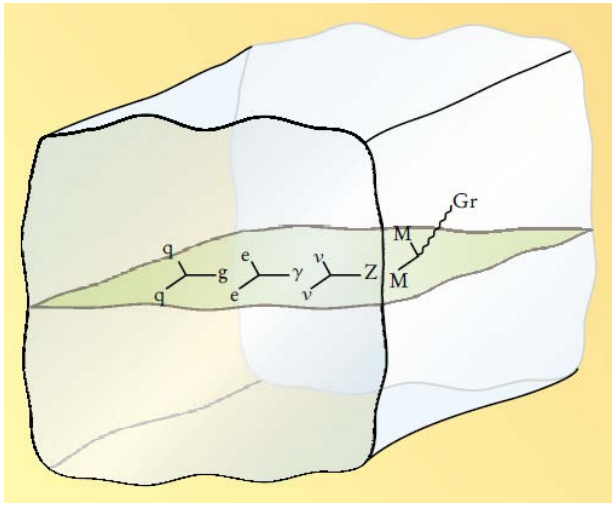
ADD and Large Extra Dimensions

Arkani–Hamed, Dimopoulos, Dvali theory

Phys. Lett. B **429**, 263–272 (1998)

Hierarchy problem: Why is gravity so much weaker? $\frac{V_G}{V_{em}} = 8 \times 10^{-37}$

Or: Why is the Planck mass M_{pl} so much bigger? $\frac{M_{\rm Pl}}{M_Z} \sim 10^{17}$



Electromagnetism, Weak and Strong forces confined in normal (3+1)-dim space

Gravity leaks out to extra *n*-dim diluting its strength

Gauss law dictates deviation from (1/*r*)-form of potential for $r << R_n$

Gravity in Extra Dimensions with compactification

Newton

$$V_{Newton}(r) = -G_3 m_1 m_2 \frac{1}{r}$$

ADD

$$V_{ADD}(r) = -G_{(3+n)} \frac{m_1 m_2}{R_{comp}^n} \frac{1}{r} \quad \text{for} \quad r > R_n$$

Gravity outside Klein radius

$$V_{ADD}(r) = -G_{(3+n)} m_1 m_2 \frac{1}{r^{n+1}} \quad \text{for} \quad r < R_n$$

Gravity inside Klein radius

derive $G_{(3+n)} = \left(R_{comp}\right)^n G_3$

$$V_{ADD}(r) = -G_3 \frac{m_1 m_2}{r} \left(\frac{R_{comp}}{r}\right)^n$$

Enhancement factor for gravity in *n* extra dimensions

A Cavendish torsion balance at 1 Å distance

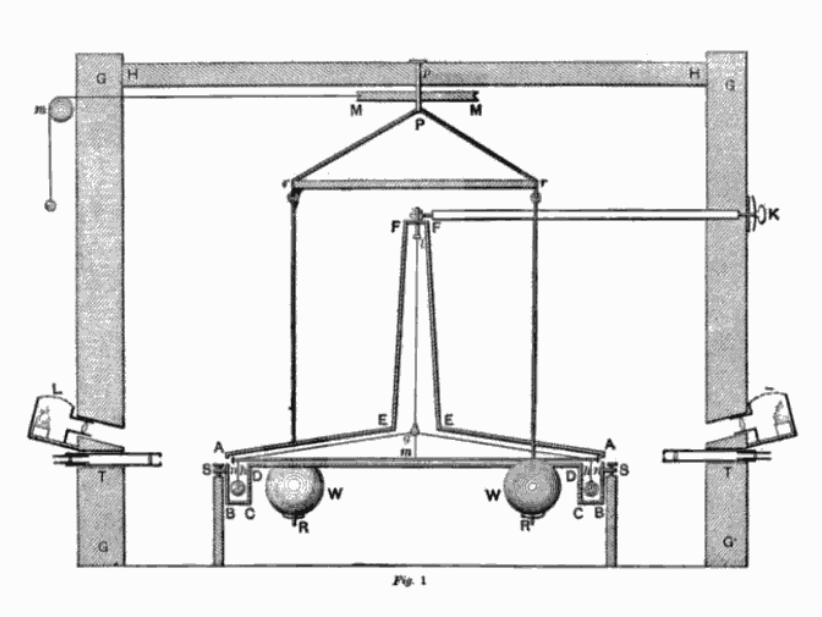
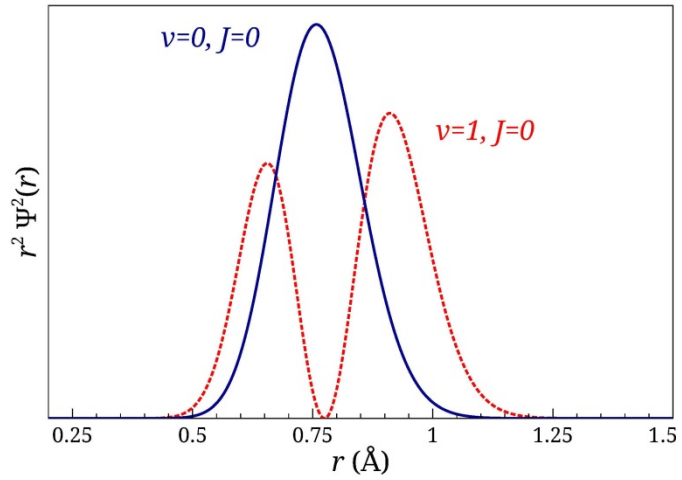


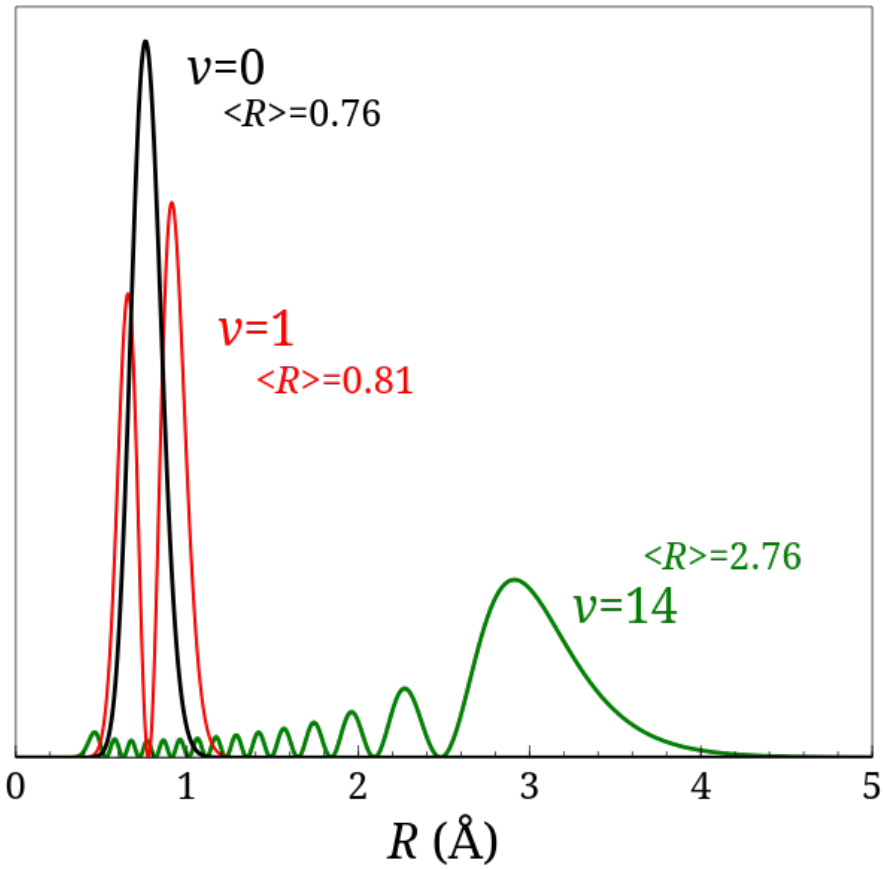
Fig. 1

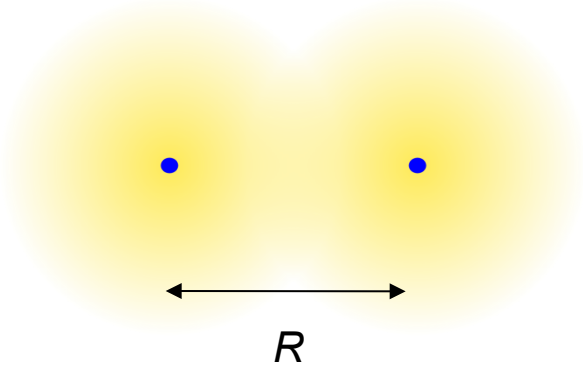
⟶ 2 protons in H_2



behave quantum mechanically

Angstrom-scale Cavendish experiment





Two protons act as Cavendish gravitating balls

Better to have large differences between quantum states

ADD in Molecules

Expectation value for the ADD-compactification in a molecule:

$$\left\langle V_{ADD}(r)\right\rangle = \alpha_G N_1 N_2 \left[R_n^n \int_0^{R_n} \Psi^*(r) \frac{1}{r^{n+1}} \Psi(r) r^2 dr + \int_{R_n}^{\infty} \Psi^*(r) \frac{1}{r} \Psi(r) r^2 dr \right]$$

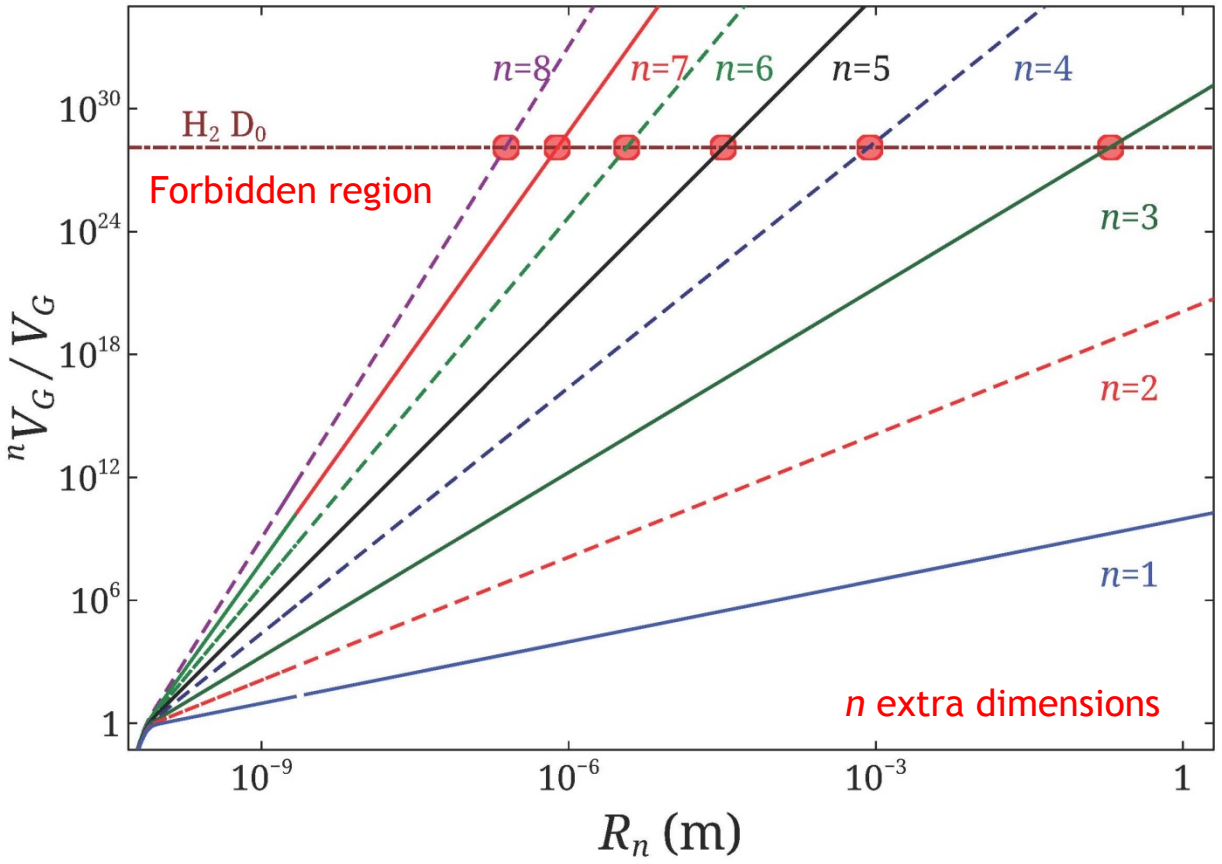
Difference between two quantum states:

$$\left\langle \Delta V_{ADD} \right\rangle = \alpha_G N_1 N_2 \left[\left\langle \frac{1}{r^{n+1}} \right\rangle_{\Psi_1} - \left\langle \frac{1}{r^{n+1}} \right\rangle_{\Psi_0} \right]$$

Test for: $\left\langle \Delta V_{ADD} \right\rangle < \delta E$

Constraints from H_2 D_0

$$\left(R_{comp}\right)^n = \frac{\delta E}{\alpha_G \hbar c N_1 N_2 \Delta \left\langle r^{-(n+1)} \right\rangle}$$



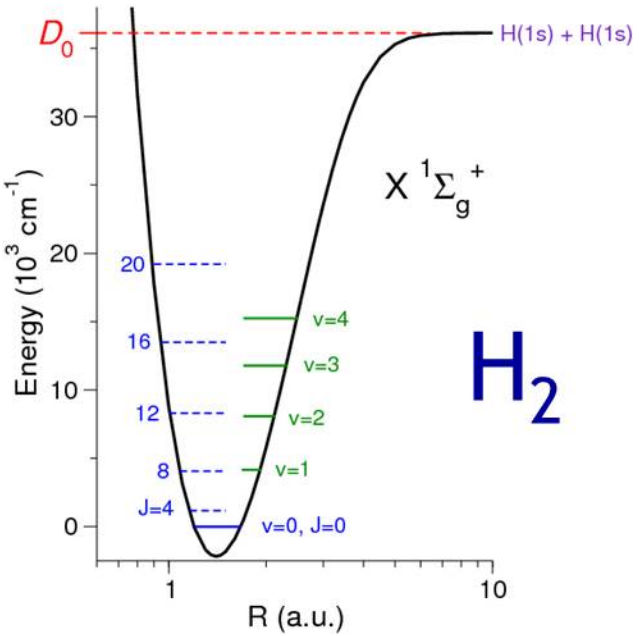
n	H_2 D_0 R_n (m)
2	2.2×10^{4}
3	1.9×10^{-1}
4	8.5×10^{-4}
5	3.2×10^{-5}
6	3.7×10^{-6}

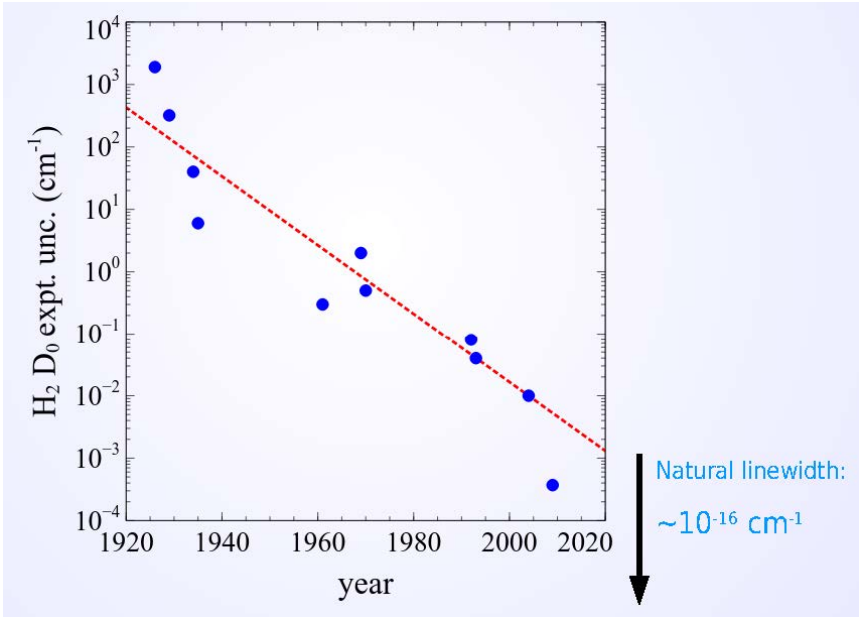
M-theory (10 dim): Compactification on μm scale !!

$R_c < 0.6$ μm

E. J. Salumbides, A. N. Schellekens, B. Gato-Rivera, W. Ubachs, New J. Phys. 17 (2015) 033015

OUTLOOK: A future molecular test system for physics





Lifetimes 10^6 seconds (!)

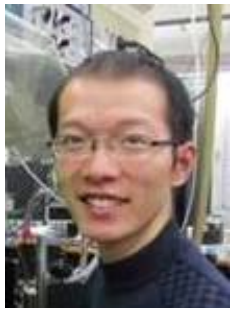
Quadrupole transitions ~ 10^{14} Hz

Possible precision 20-digit

There is room at the bottom guys

Thanks & Acknowledgement


Edcel Salumbides

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