Molecules and electronic, vibrational and rotational structure

Max Born
Nobel 1954

Robert Oppenheimer

Gerhard Herzberg
Nobel 1971
Hamiltonian for a molecule

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

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

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

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

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

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

Then:

\[ \nabla_i^2 \psi_{\text{el}}(\vec{r}_i; \vec{R}) \chi_{\text{nuc}}(\vec{R}) = \chi_{\text{nuc}}(\vec{R}) \nabla_i^2 \psi_{\text{el}}(\vec{r}_i; \vec{R}) \]

\[ \nabla_A^2 \psi_{\text{el}} \chi_{\text{nuc}} = \psi_{\text{el}} \nabla_A^2 \chi_{\text{nuc}} + 2(\nabla_A \psi_{\text{el}}) (\nabla_A \chi_{\text{nuc}}) + \nabla_A^2 \psi_{\text{el}} \]

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

\[ H \Psi_{\text{mol}} = \chi_{\text{nuc}} \left\{ -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 + \sum_{i>j} \frac{e^2}{4\pi\varepsilon_0 r_{ij}} - \sum_{A,i} \frac{Z_A e^2}{4\pi\varepsilon_0 r_{Ai}} \right\} \psi_{\text{el}} + \psi_{\text{el}} \left\{ \sum_{A>B} \frac{Z_A Z_B e^2}{4\pi\varepsilon_0 |R_A - R_B|} - \sum_A \frac{\hbar^2}{2M_A} \nabla_A^2 \right\} \chi_{\text{nuc}} = E_{\text{total}} \Psi_{\text{mol}} \]

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

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

Solve the electronic problem for each \( R \) and insert result \( E_{\text{el}} \) in wave function.

This yields a wave equation for the nuclear motion:

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

The previous analysis yields:

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

This is a Schrödinger equation with a potential energy:

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

Typical potential energy curves in molecules

nuclear repulsion  chemical binding

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

\[
- \sum_A \frac{\hbar^2}{2M_A} \nabla^2_A \chi_{\text{nuc}}(\vec{R}) + V(\vec{R}) \chi_{\text{nuc}}(\vec{R}) = E \chi_{\text{nuc}}(\vec{R})
\]
Quantum mechanical two-particle problem
Transfer to centre-of-mass system

\[ \mu = \frac{M_A M_B}{M_A + M_B} \]

Single-particle Schrödinger equation

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

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-known equation with solutions:

Angular momentum operators
Spherical harmonic wave functions!
Angular momentum in a molecule

Solution:
\[ \hat{N}^2 |N, M\rangle = \hbar^2 N(N + 1) |N, M\rangle \]
\[ N_z |N, M\rangle = \hbar M |N, M\rangle \]
with
\[ N = 0, 1, 2, 3..., \]
\[ M = -N, -N + 1, ..., N \]

And angular wave function
\[ |N, M\rangle = Y_{NM}(\theta, \phi) \]

Hence the wave function of the molecule:
\[ \chi_{\text{nuc}}(R, \theta, \phi) = \Xi(R)Y_{NM}(\theta, \phi) \]

Reduction of molecular Schrödinger equation

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

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

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

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

Deduce $R_e$ from spectroscopy

isotope effect
Vibrational motion

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

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 \( \rho = R - R_e \)

\[
V(R) = V(R_e) + \frac{dV}{dR} \bigg|_{R_e} \rho + \frac{1}{2} \frac{d^2V}{dR^2} \bigg|_{R_e} \rho^2 + ...
\]

\( V(R_e) = 0 \) \hspace{1cm} \text{by choice}

\[
\frac{dV}{dR} \bigg|_{R_e} = 0 \quad \text{at the bottom of the well}
\]

Hence: \( V(R) = k(R - R_e)^2 \) harmonic potential
Vibrational motion

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

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

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

with: \( \alpha = \frac{\mu \omega_e}{\hbar} \) and \( \omega_e = \sqrt{\frac{k}{\mu}} \)

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:

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

Vibrational energies in the H\textsubscript{2}-molecule
## Energy levels in a molecule: general structure

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[ \Psi_B \]

\[ J \quad v=0 \]
\[ J \quad v=1 \]
\[ J \quad v=2 \]

\[ \Psi_A \]

\[ J \quad v=0 \]
\[ J \quad v=1 \]
\[ J \quad v=2 \]

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

\[ B = \frac{\pi e^2}{3\varepsilon_0 \hbar^2} |\mu_{ij}|^2 \]

\[ \Psi_{\text{mol}}(\vec{r}_i, \vec{R}_A) = \psi_{\text{el}}(\vec{r}_i; \vec{R}) \psi_{\text{vib}}(\vec{R}) \]

Dipole transition between two states

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

Two different types of transitions

\[ \mu_{if} = \int \psi'_e \psi'_v \mu_e + \mu_N \psi''_e \psi''_v d\tau = \]

\[ \int \left( \int \psi'_e \mu_e \psi'_v d\vec{r} \right) \psi''_v \psi''_v d\vec{R} + \]

\[ \int \psi'_e \psi'_v d\vec{r} \int \psi''_v \mu_N \psi''_v d\vec{R} \]

Electronic transitions

Rovibrational transitions
The Franck-Condon principle for electronic transitions in molecules

1st term:

\[ \mu_{if} = \int \left( \int \psi_{el}' \mu \psi_{el}'' d\bar{R} \right) \psi_{vib}' \psi_{vib}'' d\bar{R} \]

Only contributions if (parity selection rule)

\[ \psi_{el}' \neq \psi_{el}'' \]

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

\[ \bar{M}_e (R) = \int \psi_{el}' \mu \psi_{el}'' d\bar{R} \]

Hence

\[ \mu_{if} = \bar{M}_e (R) \int \psi_{vib}' \psi_{vib}'' d\bar{R} \]

Intensity of electronic transitions

\[ I \propto |\mu_{if}|^2 \propto \left| \int \psi_{vib}' \psi_{vib}'' d\bar{R} \right|^2 \propto \langle \psi' | \psi'' \rangle^2 \]

Intensity proportional to the square of the wave function overlap
Rotational transitions in molecules

2\textsuperscript{nd} 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.

\[ \bar{\mu} = \mu_0 \begin{bmatrix} \sin \theta \cos \phi \\ \sin \theta \sin \phi \\ \cos \theta \end{bmatrix} \propto \mu_0 Y_{1m} \]

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

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

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:

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

Ground state with \( N'' \) and excited \( N' \)
Absorption in rotational ladder: \( N' = N'' + 1 \)

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

Spacing between lines \( \sim 2B \)
Rotational spectrum in a diatomic molecule

Ground state with \( N'' \) and excited \( N' \)
Absorption in rotational ladder: \( N' = N'' + 1 \)

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

Spacing between lines \( \sim 2B \)

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

\[ \mu_{if} = \int \psi'_{el} \psi''_{el} d\vec{r} \int \psi'_{vib} \mu_N \psi''_{vib} d\vec{R} \]

Within a certain electronic state:

\[ \psi'_{el} = \psi''_{el} \rightarrow \int \psi'_{el} \psi''_{el} d\vec{r} = 1 \]

Line intensity:

\[ \mu_{if} = \langle v' | \mu_{vib} | v'' \rangle \]

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.

\[ \mu_{if} = \langle v' \left| \frac{d}{dR} \vec{u} \right| v'' \rangle_{R_e} \rho \langle v'' \rangle \propto \langle v' | \rho | v'' \rangle \]

Dipole moment should vary with Displacement \( \rightarrow \) vibrational spectrum
Vibrational transitions in molecules

Permanent and induced dipole moments:

\[
\mu_{if} = \langle v'|\mu_{\text{vib}}|v''\rangle = \langle v'|a\rho + b\rho^2|v''\rangle
\]

First order: the vibrating dipole moment

\[
\mu_{if} = \langle v'|\mu_{\text{vib}}|v''\rangle \propto \langle v'|\rho|v''\rangle
\]

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: \(\Delta v = v' - v = \pm 1\)

Homonuclear molecule

\[
\mu_N = \sum_A eZ_A \bar{R}_A = eZ_A(\bar{R}_A - \bar{R}_A) = 0
\]

For all derivatives
No vibrational dipole spectrum

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

\( \nu'' \) (ground) to \( \nu' \) (excited)

\[ \sigma(\nu' - \nu'') = \sigma_0 + F_{\nu'}(N') - F_{\nu''}(N'') \]
with

\[ \sigma_0 = G(\nu') - G(\nu'') \]

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

Transitions

R-branch \((N' = N'' + 1)\) - neglect \(D\)

\[ \sigma_R = \sigma_0 + 2B_{\nu'} + (3B_{\nu'} - B_{\nu''})N + (B_{\nu'} - B_{\nu''})N^2 \]

For \( B_{\nu'} = B_{\nu''} \)

\[ \sigma_R = \sigma_0 + 2B_{\nu'}(N + 1) \]

P-branch \((N' = N'' - I)\) - neglect \(D\)

\[ \sigma_P = \sigma_0 - (B_{\nu'} + B_{\nu''})N + (B_{\nu'} - B_{\nu''})N^2 \]

For \( B_{\nu'} = B_{\nu''} \)

\[ \sigma_R = \sigma_0 + 2B_{\nu'}(N + 1) \]
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 \( \rightarrow \) governed by the Franck-Condon principle

Rotations \( \rightarrow \) governed by angular momentum selection rules

Transition frequencies

\[ v = T'' - T''\]

\[ T'' = T_B + G' (v') + F'_v (N') \]

\[ T'' = T_A + G'' (v'') + F''_v (N'') \]

R and P branches can be defined in the same way

\[ \sigma_R = \sigma_0 + 2B_v' + (3B_v' - B_v'') N + (B_v' - B_v'') N^2 \]

\[ \sigma_P = \sigma_0 - (B_v' + B_v'') N + (B_v' - B_v'') N^2 \]
\[ \sigma_R = \sigma_0 + 2B_v' + (3B_v' - B_v'')N + (B_v' - B_v'')N^2 \]
\[ \sigma_P = \sigma_0 - (B_v' + B_v'')N + (B_v' - B_v'')N^2 \]

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

- no line for \( m=0 \); band gap
- there is always a band head, in one branch
Probability of finding a molecule in a vibrational quantum state:

\[
P(v) = \frac{e^{-E(v)/kT}}{\sum_v e^{-E(v)/kT}} \quad \frac{-\omega_e(v+1/2)}{kT} = \frac{1}{Z} e^{-\omega_e v_T / kT}
\]

Boltzmann distribution

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:

\[
\frac{\Delta v}{v} = K_\mu \frac{\Delta \mu}{\mu}
\]

Calculation for Lyman-α transition

\[
v = \frac{E_2 - E_1}{\hbar} = \frac{3}{4} R_\infty c \left( \frac{\mu_{\text{red}}}{m_e} \right)
\]

with

\[
\frac{\mu_{\text{red}}}{m_e} = \frac{1}{m_e} \frac{M_p m_e}{M_p + m_e} = \frac{M_p / m_e}{1 + M_p / m_e} = \frac{\mu}{1 + \mu}
\]

So (note energy scale drops out!):

\[
\frac{\Delta v}{v} = \frac{\Delta(E_2 - E_1)}{E_2 - E_1} = \frac{\frac{\mu + \Delta \mu}{1 + \mu + \Delta \mu} - \frac{\mu}{1 + \mu}}{\mu / (1 + \mu)} = \frac{\Delta \mu / \mu}{1 + \mu + \Delta \mu} = K_\mu \frac{\Delta \mu}{\mu}
\]

\[
\rightarrow K_\mu = \frac{1}{1 + \mu + \Delta \mu} \approx 5.4 \times 10^{-4}
\]
Isotope effects in molecules + sensitivity for $\mu$-variation

Electronic

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

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

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 $\mu$-variation

Vibrational energy:

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

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

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

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

So:

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

For ALL vibrational transitions
Isotope effects in molecules + sensitivity for $\mu$-variation

Rotational energy: 

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

$K$-coefficient for purely rotational transition:

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

So:

$$K_{\mu} = -1$$
Isotope effects in molecules + sensitivity for $\mu$-variation

For $H_2$

$E_{electronic}$

$E_{vibrational}$

$E_{rotational}$

$E_{total}$

Lyman bands
$B^1\Sigma^+_u - X^1\Sigma^+_g$

Werner bands
$C^1\Pi_u - X^1\Sigma^+_g$

94 nm

110 nm
$K_i$ different for $H_2$ lines
**Electronic spectra of $H_2$**

**Composition of the universe:**
- 80% hydrogen $H/H_2$
- 20% helium
- <0.1% other elements

$H$ (Lyman-$\alpha$) $\sim 121$ nm

$H_2$, Lyman en Werner BANDS
$\sim 90 - 110$ nm
Extreme Ultraviolet Wavelengths
Empirical search for a change in $\mu$

- Spectroscopy
- Compare $H_2$ spectra in different epochs:

\[ \frac{\lambda_i}{\lambda_i^0} \equiv 1 + z_i \]

- Atmospheric transmission only for $z>2$
Q2348-011
$z = 2.42$

Magnitude
18.4

1 arcsecond
UVES:
Ultraviolet - Visual Echelle Spectrograph
Empirical search for a change in $\mu$: quasars
J2123 from HIRES-Keck at Hawaii (normalized)

Resolution 110000; $z_{\text{abs}}=2.0593$

$H_2$

Keck telescope, Hawaii
J2123, \( z_{\text{abs}} = 2.0593426 \), H2 lines
First Constraint on Cosmological Variation of the Proton-to-Electron Mass Ratio from Two Independent Telescopes

F. van Weerdeburg, M. T. Murphy, A. L. Malec, L. Kaper, and W. Ubachs

1Institute for Lasers, Life and Biophotonics, VU University Amsterdam, de Boelelaan 1081, 1081 HV Amsterdam, The Netherlands
2Astronomical Institute Anton Pannekoek, Universiteit van Amsterdam, 1098 SJ Amsterdam, The Netherlands
3Centre for Astrophysics and Supercomputing, Swinburne University of Technology, Melbourne, Victoria 3122, Australia
(Received 3 March 2011; published 6 May 2011)

Keck:
\[ \Delta \mu/\mu = (5.6 \pm 5.5_{\text{stat}} \pm 2.9_{\text{syst}}) \times 10^{-6} \]

VLT:
\[ \Delta \mu/\mu = (8.5 \pm 3.6_{\text{stat}} \pm 2.2_{\text{syst}}) \times 10^{-6} \]
## How much H2 at high redshift?

<table>
<thead>
<tr>
<th>Quasars</th>
<th>$z_{abs}$</th>
<th>$z_{em}$</th>
<th>RA</th>
<th>Decl.</th>
<th>$N(H_2)$</th>
<th>$N(HD) \cdot N(HI)$</th>
<th>$R_{mag}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q0347−383</td>
<td>3.02</td>
<td>3.21</td>
<td>03:49:43.64</td>
<td>−38:10:30.6</td>
<td>14.5</td>
<td>20.6</td>
<td>17.48</td>
<td>[7, 19]</td>
</tr>
<tr>
<td>Q0405−443</td>
<td>2.59</td>
<td>3.00</td>
<td>04:07:18.08</td>
<td>−44:10:13.9</td>
<td>18.2</td>
<td>20.9</td>
<td>17.34</td>
<td>[7, 19]</td>
</tr>
<tr>
<td>Q0528−250</td>
<td>2.81</td>
<td>2.81</td>
<td>05:30:07.95</td>
<td>−25:03:29.7</td>
<td>18.2</td>
<td>21.1</td>
<td>17.37</td>
<td>[19]</td>
</tr>
<tr>
<td>J2123−005</td>
<td>2.06</td>
<td>2.26</td>
<td>21:23:29.46</td>
<td>−00:50:52.9</td>
<td>17.6</td>
<td>19.2</td>
<td>15.83</td>
<td>[15]</td>
</tr>
<tr>
<td>Q0013−004</td>
<td>1.97</td>
<td>2.09</td>
<td>00:16:02.40</td>
<td>−00:12:25.0</td>
<td>18.9</td>
<td>20.8</td>
<td>17.89</td>
<td>[40]</td>
</tr>
<tr>
<td>HE0027−184</td>
<td>2.42</td>
<td>2.55</td>
<td>00:30:23.62</td>
<td>−18:19:56.0</td>
<td>17.3</td>
<td>21.7</td>
<td>17.37</td>
<td>[33]</td>
</tr>
<tr>
<td>Q0551−366</td>
<td>1.96</td>
<td>2.32</td>
<td>05:52:46.18</td>
<td>−36:37:27.5</td>
<td>17.4</td>
<td>20.5</td>
<td>17.79</td>
<td>[41]</td>
</tr>
<tr>
<td>J1041+320</td>
<td>2.63</td>
<td>2.70</td>
<td>08:12:40.6</td>
<td>+32:08:08</td>
<td>19.9</td>
<td>15.4</td>
<td>21.4</td>
<td>17.88</td>
</tr>
<tr>
<td>Q0841+129</td>
<td>2.37</td>
<td>2.48</td>
<td>08:44:24.24</td>
<td>+12:45:46.5</td>
<td>14.5</td>
<td>20.6</td>
<td>17.64</td>
<td>[42]</td>
</tr>
<tr>
<td>Q1232+082</td>
<td>2.34</td>
<td>2.57</td>
<td>12:34:37.58</td>
<td>+07:58:43.6</td>
<td>19.7</td>
<td>15.5</td>
<td>20.9</td>
<td>18.40</td>
</tr>
<tr>
<td>J1237+064</td>
<td>2.69</td>
<td>2.78</td>
<td>12:37:14.60</td>
<td>+06:47:59.5</td>
<td>19.2</td>
<td>14.5</td>
<td>20.0</td>
<td>18.21</td>
</tr>
<tr>
<td>Q1331+170</td>
<td>1.78</td>
<td>1.78</td>
<td>13:33:35.81</td>
<td>+16:49:03.7</td>
<td>19.7</td>
<td>14.8</td>
<td>21.2</td>
<td>16.26</td>
</tr>
<tr>
<td>Q1439+113</td>
<td>2.42</td>
<td>2.58</td>
<td>14:39:12.04</td>
<td>+11:17:40.5</td>
<td>19.4</td>
<td>14.9</td>
<td>20.1</td>
<td>18.07</td>
</tr>
<tr>
<td>Q1441+272</td>
<td>4.22</td>
<td>4.42</td>
<td>14:43:31.18</td>
<td>+27:24:36.4</td>
<td>18.3</td>
<td>21.0</td>
<td>18.81</td>
<td>[38]</td>
</tr>
<tr>
<td>Q1444+014</td>
<td>2.08</td>
<td>2.21</td>
<td>14:46:53.04</td>
<td>+01:13:56.0</td>
<td>18.3</td>
<td>20.1</td>
<td>18.10</td>
<td>[47]</td>
</tr>
<tr>
<td>Q2318−111</td>
<td>1.99</td>
<td>2.56</td>
<td>23:21:28.69</td>
<td>−10:51:22.5</td>
<td>15.5</td>
<td>20.7</td>
<td>17.67</td>
<td>[33]</td>
</tr>
<tr>
<td>Q2343+125</td>
<td>2.43</td>
<td>2.52</td>
<td>23:46:25.42</td>
<td>+12:47:43.9</td>
<td>13.7</td>
<td>20.4</td>
<td>20.18</td>
<td>[22, 48]</td>
</tr>
<tr>
<td>Q2348−011</td>
<td>1.42</td>
<td>3.02</td>
<td>23:50:57.87</td>
<td>−00:52:09.9</td>
<td>18.4</td>
<td>20.5</td>
<td>18.31</td>
<td>[23, 44]</td>
</tr>
</tbody>
</table>

**Notes:**
- VLT 2013
- Done 2012
The rise of a giant

39m dish

Cerro Amazones

The European Extremely Large Telescope (Artist’s Impression)
Outlook: More sensitive molecules

Quantum tunneling

\[ K = -4.2 \]
Outlook: More sensitive molecules

Quantum tunneling

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

Paul Jansen, Li-Hong Xu, Isabelle Kleiner, Wim Ubachs, and Hendrick L. Bethlem
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

PKS-1830-211
at $z=0.88582$
(7 Gyrs look-back)

$\Delta \mu/\mu = (-0.1 \pm 7.6_{\text{stat}}) \times 10^{-8}$