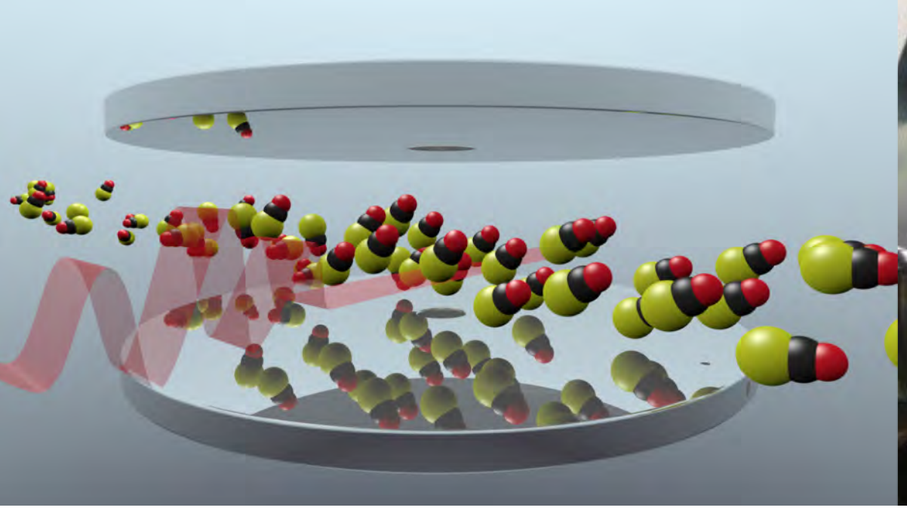
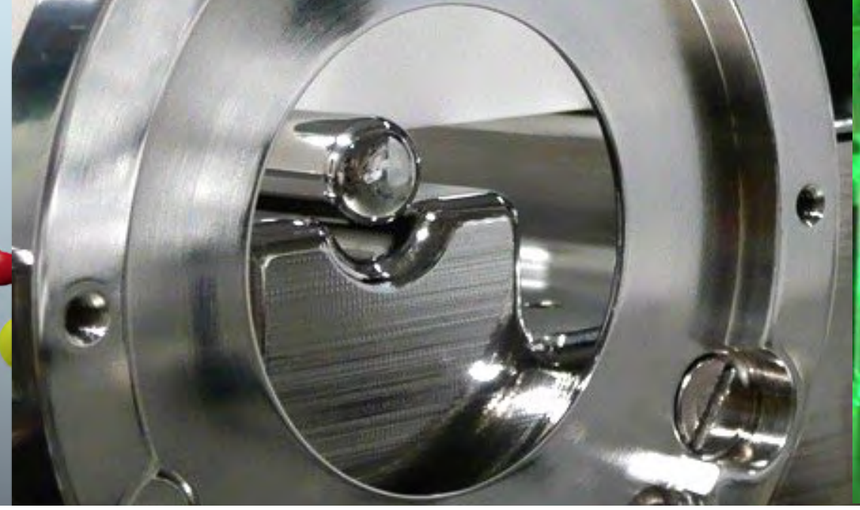
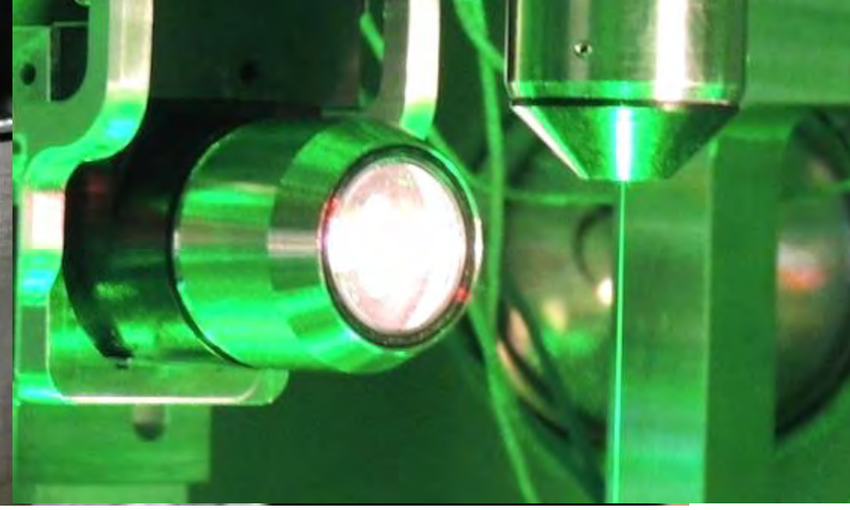




Molecular Sciences

Introduction of concepts and the basics of molecular physics

Jochen Küpper

Center for Free-Electron Laser Science, Deutsches Elektronen-Synchrotron DESY, Hamburg

Department of Physics & Department of Chemistry, Universität Hamburg

The Hamburg Center for Ultrafast Imaging, Universität Hamburg

3. & 7. August 2017

based on the UHH master module “The Basis of Modern Molecular Physics”

CUI THE HAMBURG CENTER FOR ULTRAFAST IMAGING

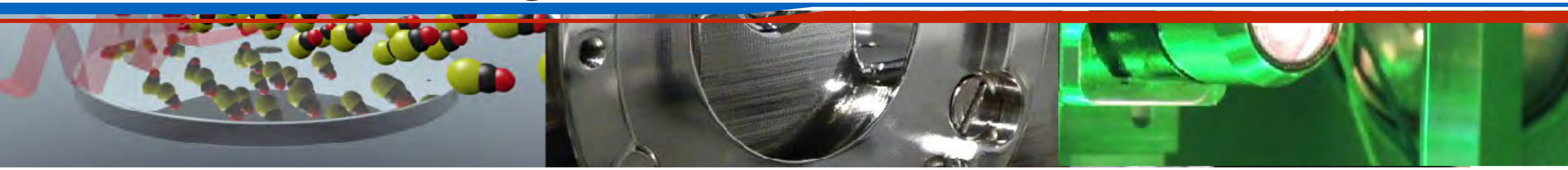
UHH Universität Hamburg
DER FORSCHUNG | DER LEHRE | DER BILDUNG

CFEL SCIENCE
Controlled Molecule Imaging

DESY

erc CoMotion
European Research Council
Established by the European Commission

Controlled Molecule Imaging
talking to molecules “at work”



Center for Free-Electron Laser Science, Deutsches Elektronen-Synchrotron DESY, Hamburg

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Universität Hamburg

CFEL SCIENCE

DESY

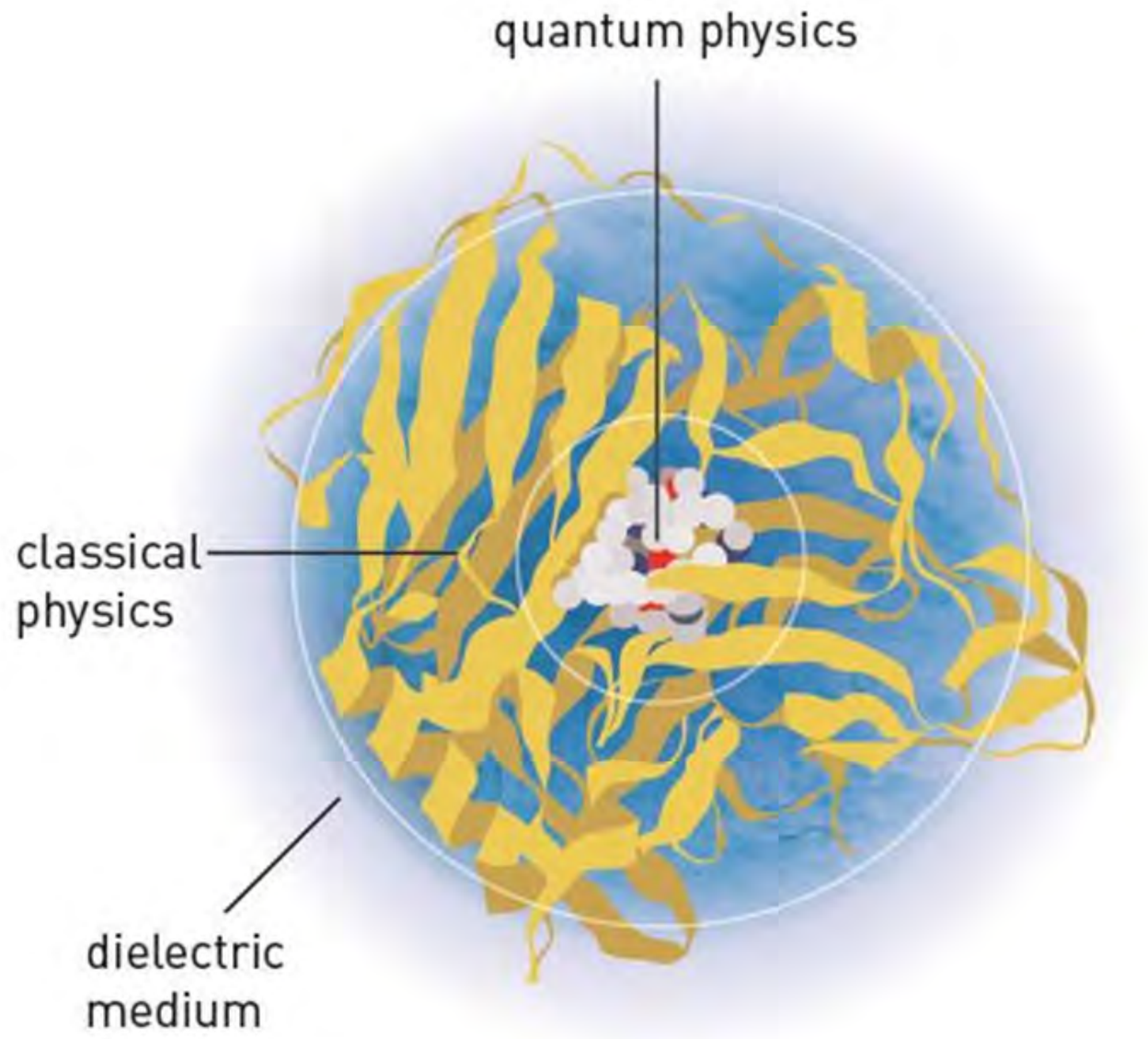
erc CoMotion European Research Council

Outline in a nutshell

1. The (quantum-mechanical) properties of isolated molecules
2. The interaction of molecules with electromagnetic fields, including the interaction with light
3. The interaction of atoms and molecules (with each other)

The Nobel Prize in Chemistry 2013

Multiscale models for complex chemical systems

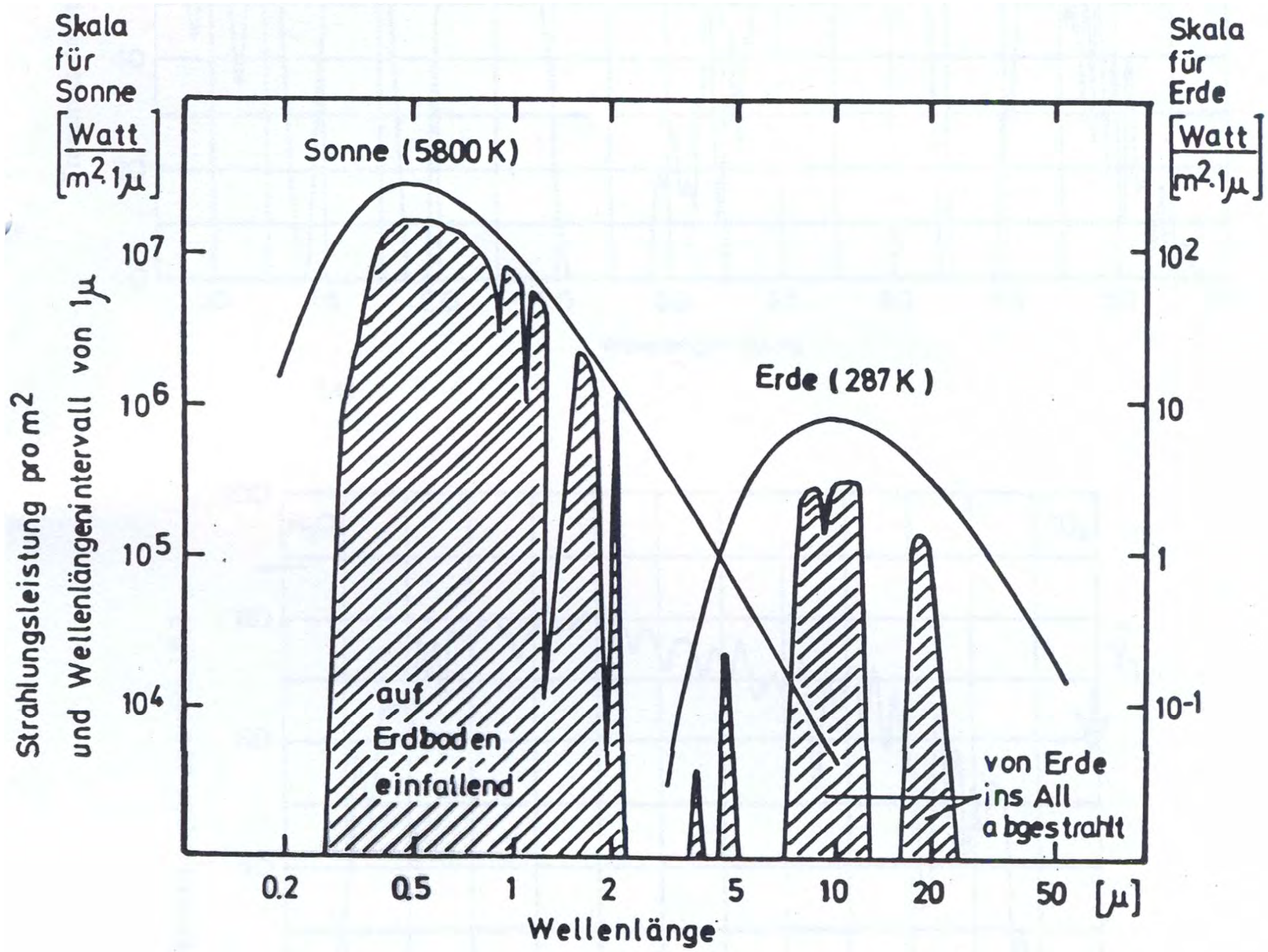


kindly provided by Professor Ulf Ryde
(Division of Theoretical Chemistry, Lund University)

http://nobelprize.org/nobel_prizes/chemistry/laureates/2013/index.html

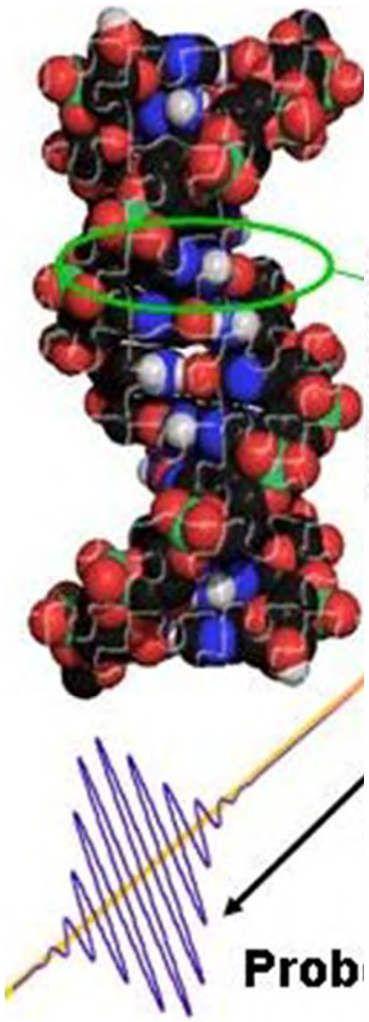
Importance of molecular structure

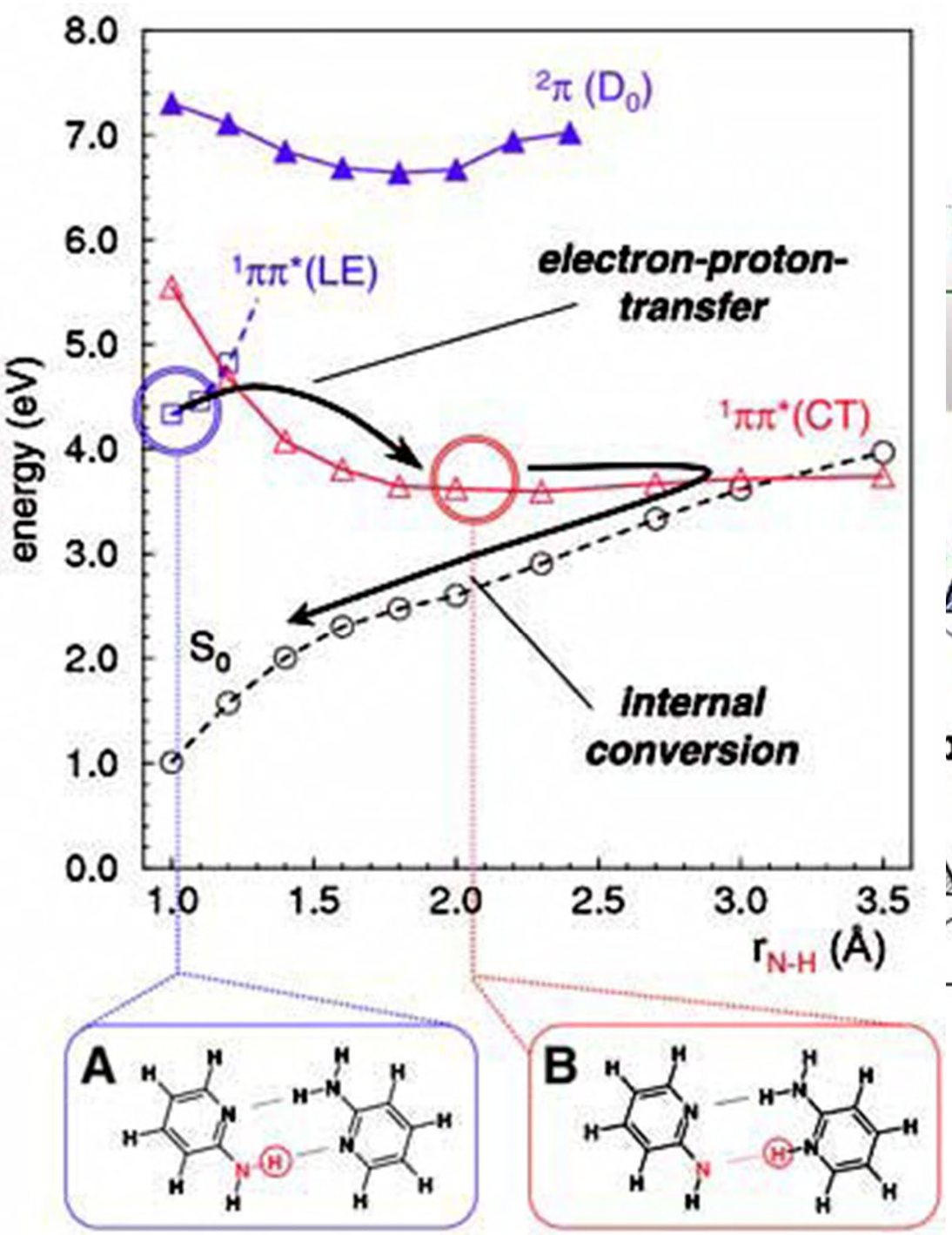
- Black-body radiation of sun and earth → greenhouse effect
- Absorption of water vapor, carbon dioxide, methane, ozone

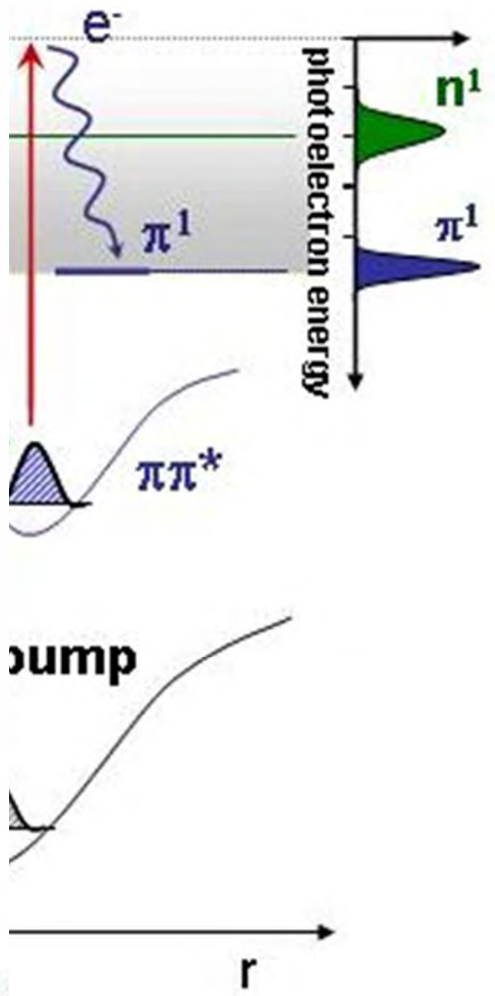


Relation between molecular structure, function and dynamics

- Efficient absorption of UV radiation by ozone via conical intersections
- But, ozone was generated in the atmosphere AFTER oxygen production had started
- How

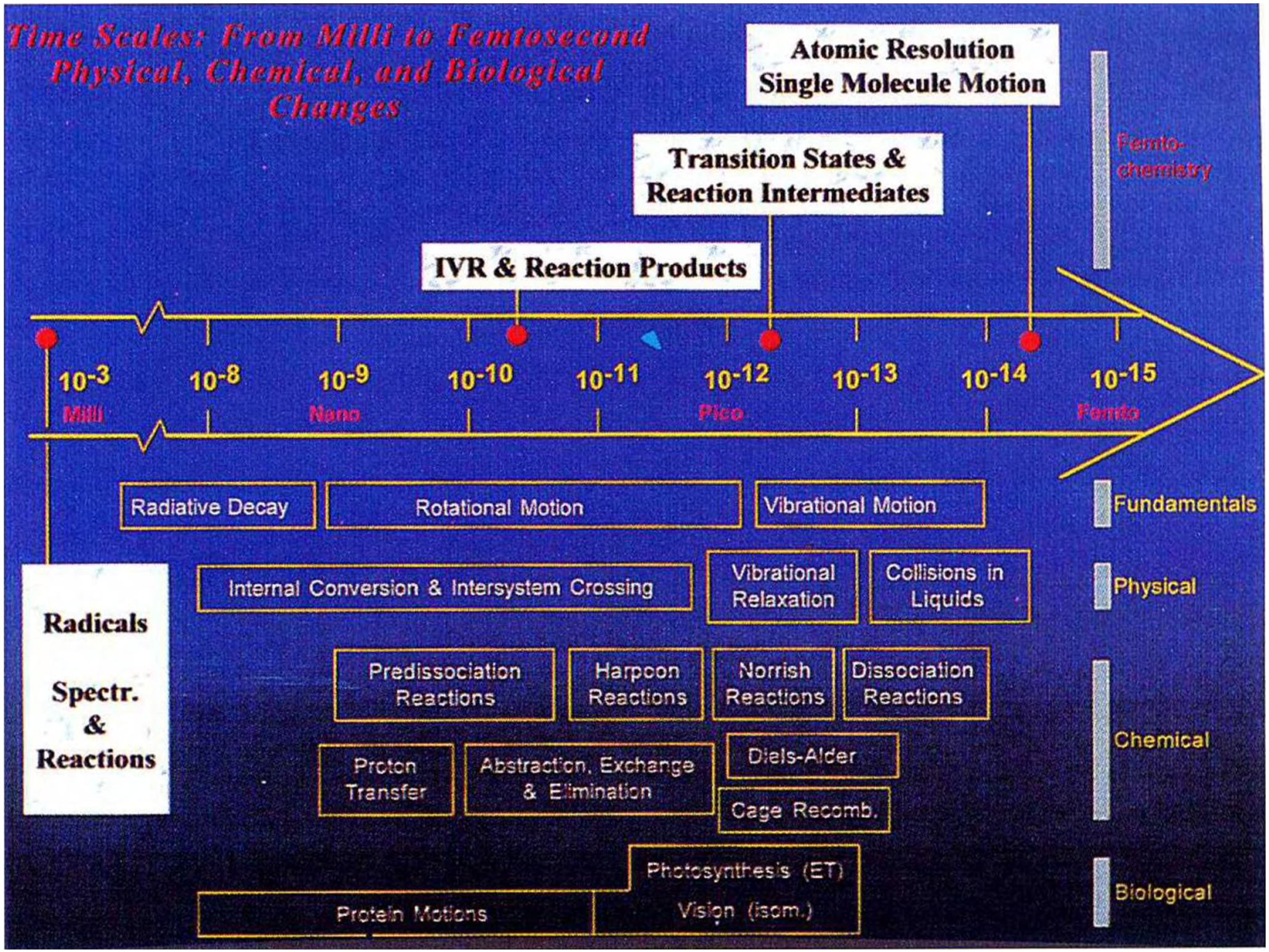




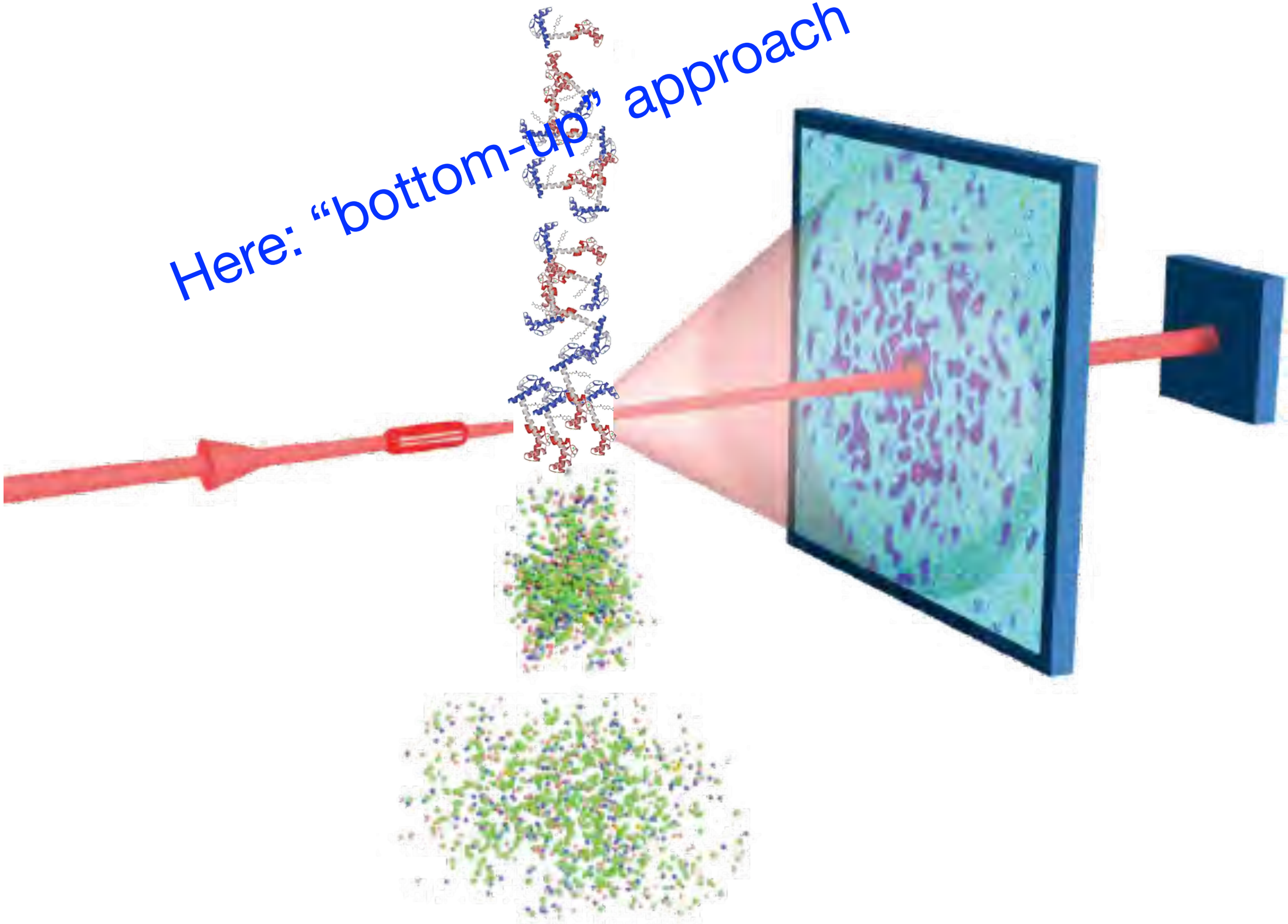


- How does molecul

Recording the molecular movie – timescales



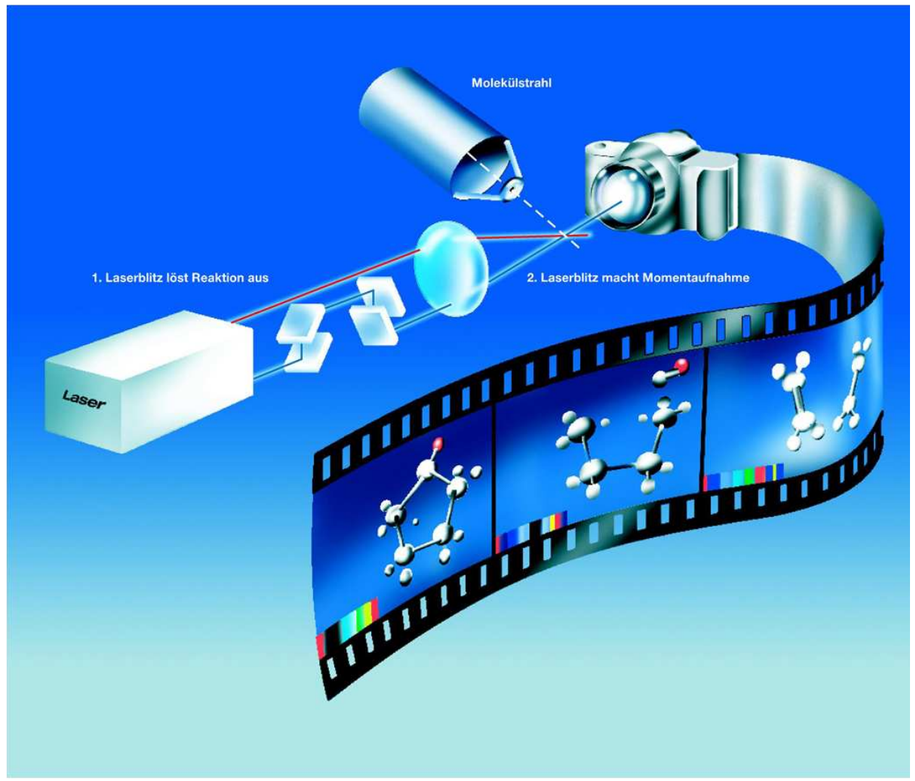
Watching chemistry
with atomic spatial (100 pm) and temporal (10 fs) resolution

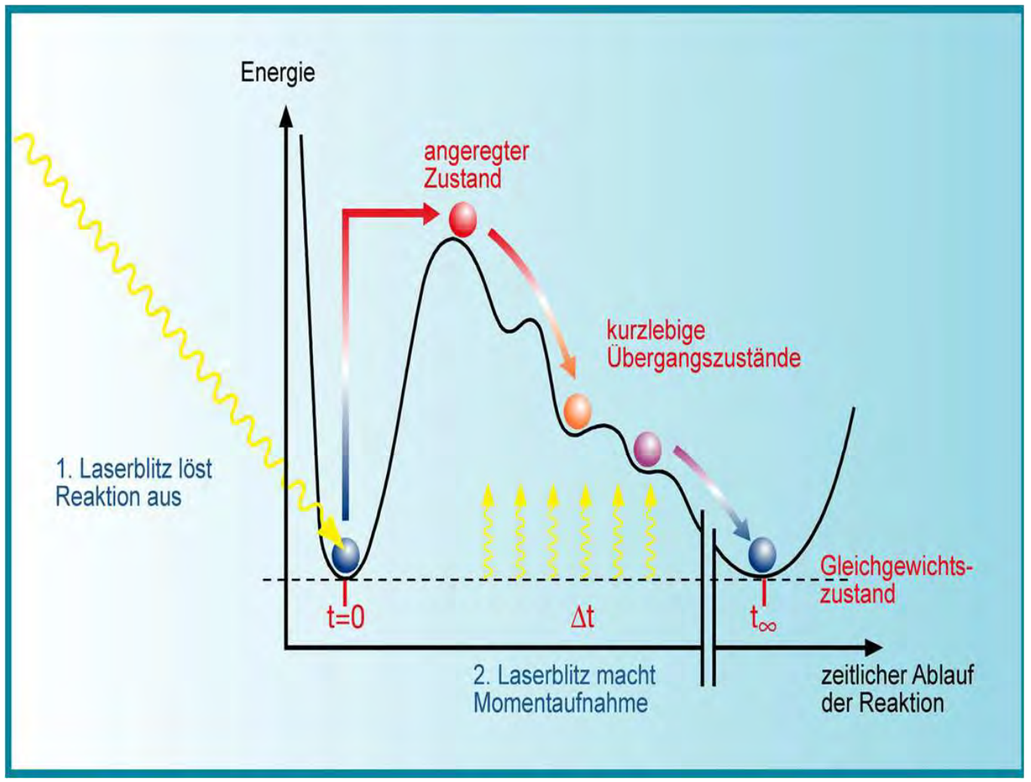


Barty, Küpper, Chapman, *Ann. Rev. Phys. Chem.* **64**, 415–435 (2013)

Recording the molecular movie – the ultimate dream

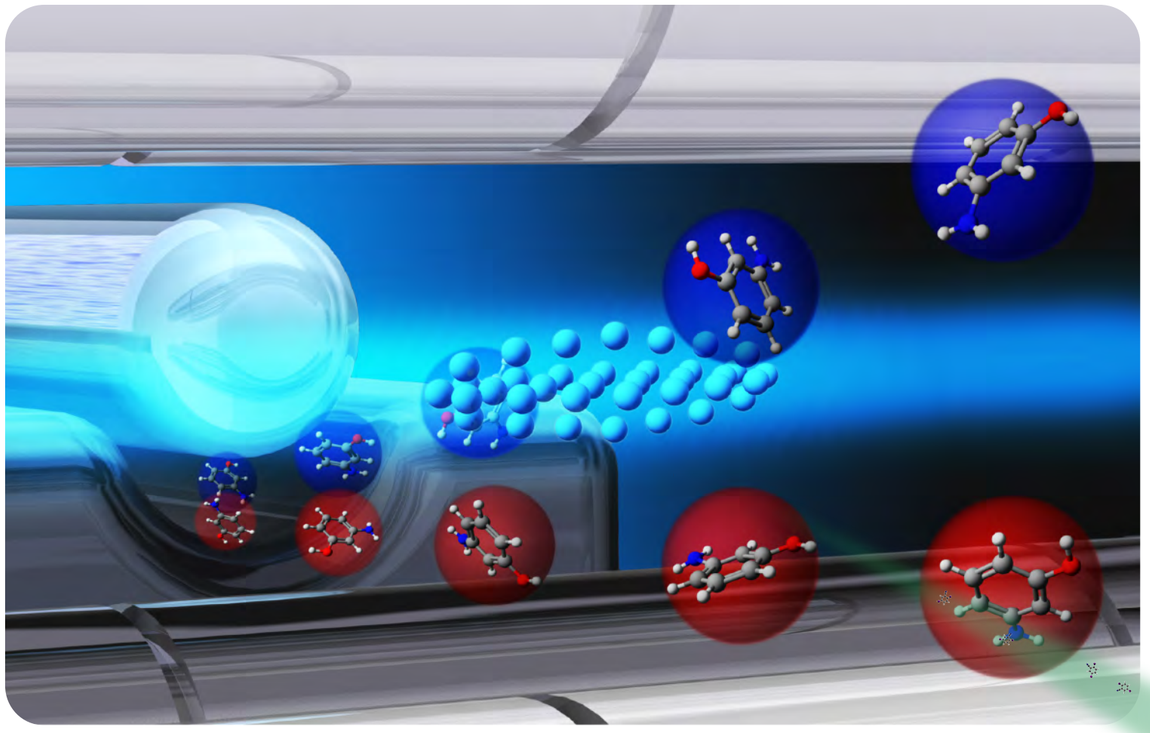
- Imaging chemical reactions of single molecules

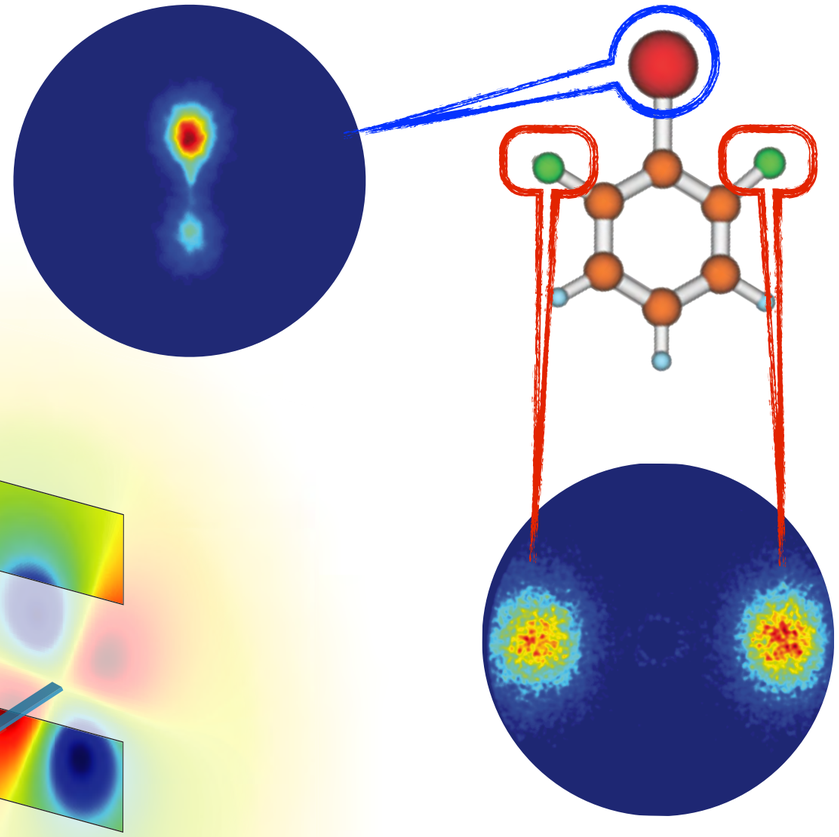


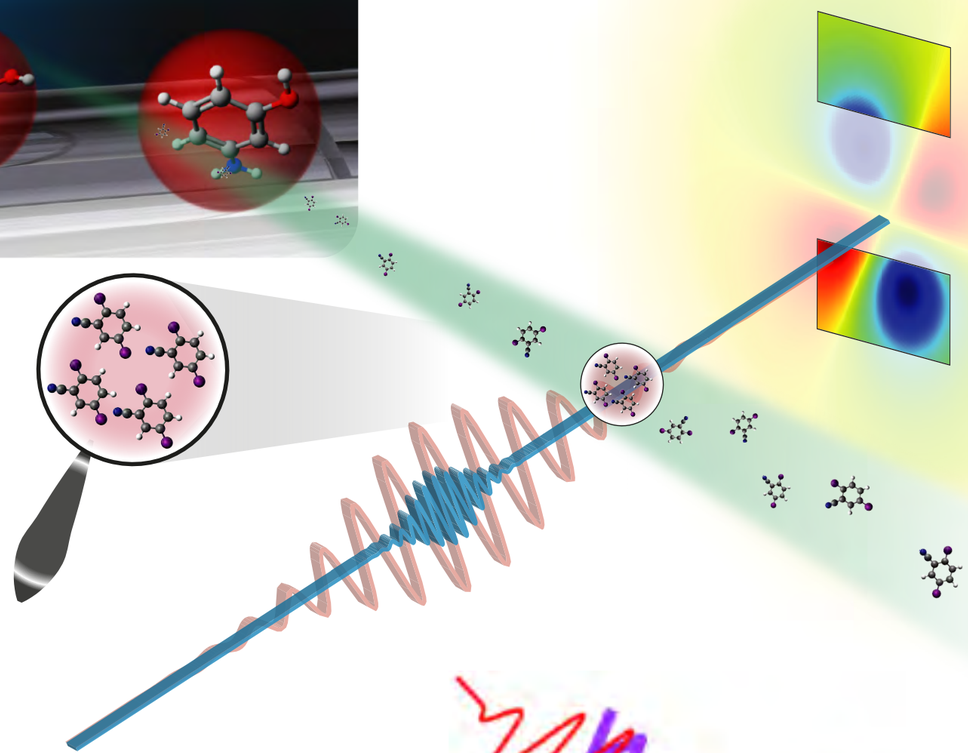


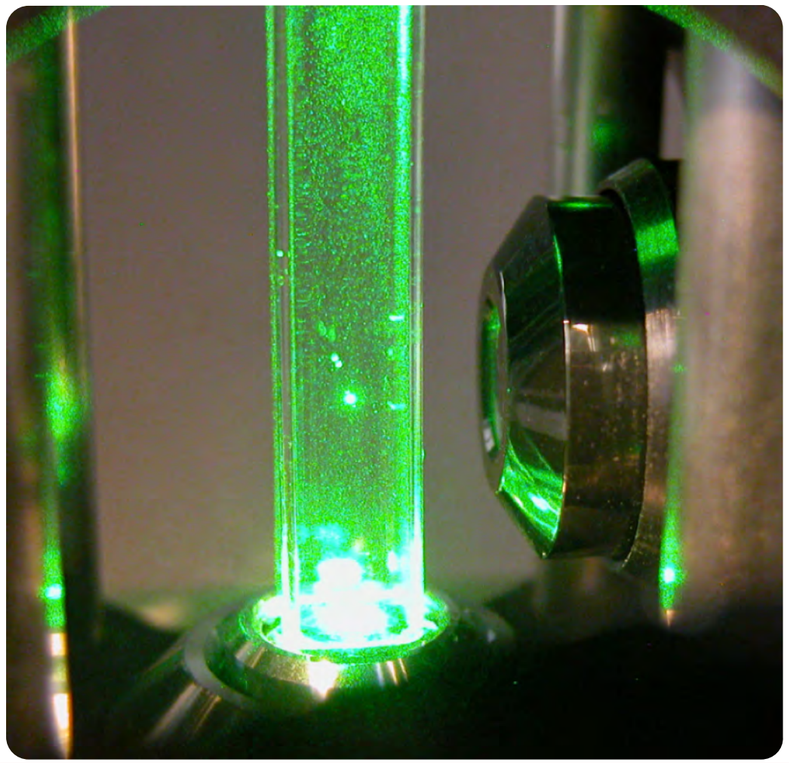
with atomic resolution in real time

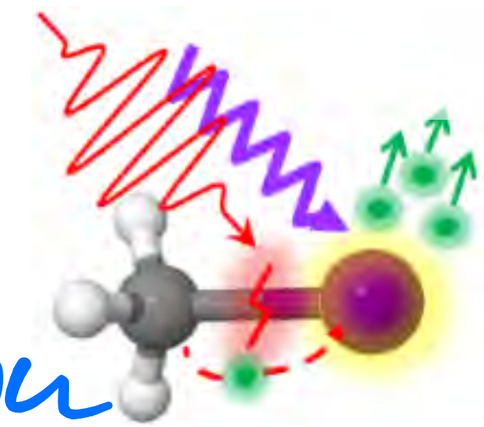
Controlled Molecule Imaging
Toward a microscopic understanding of molecules at work

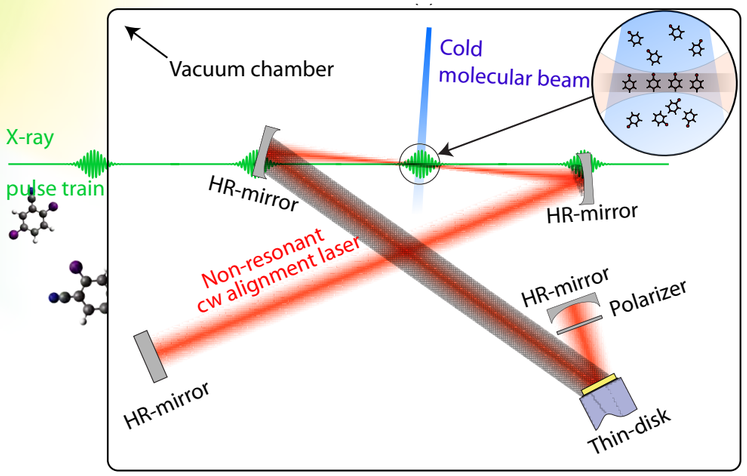


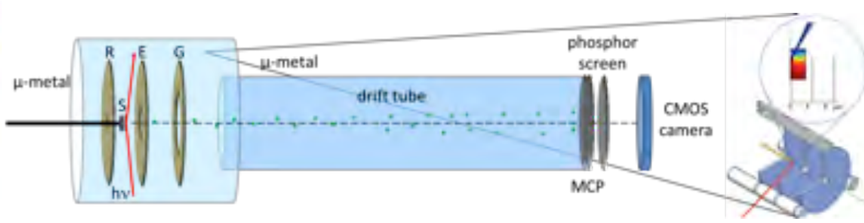








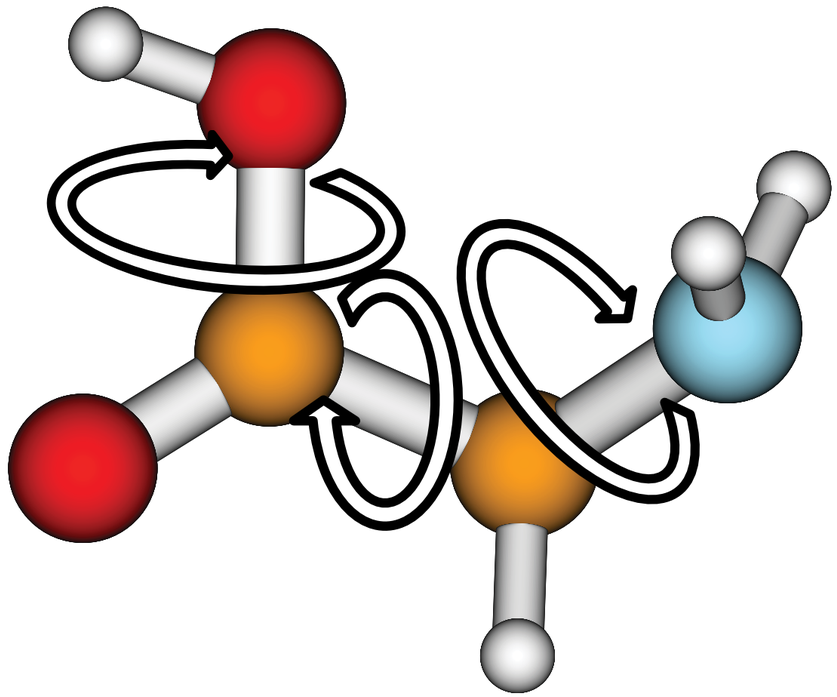


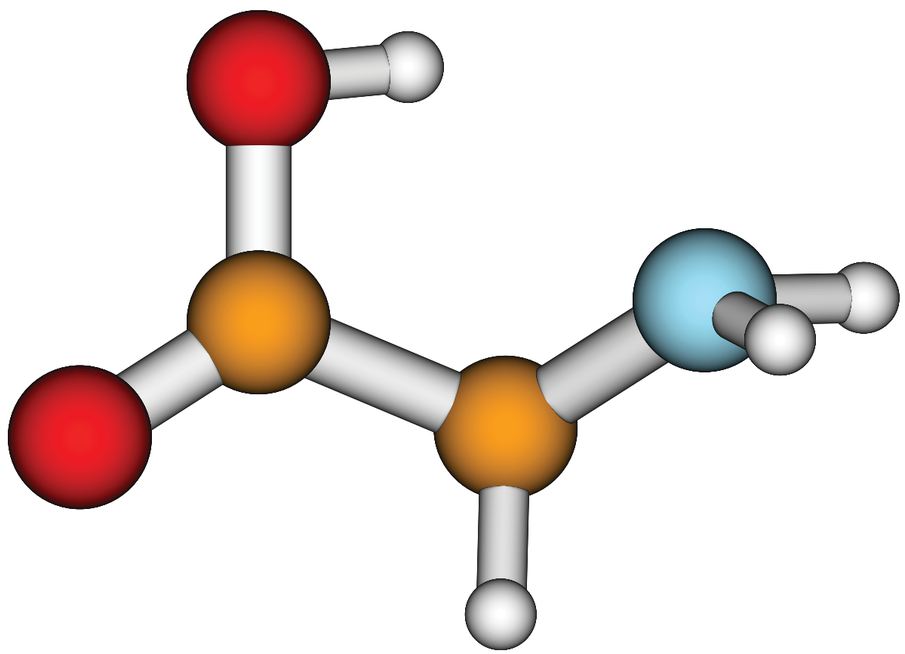


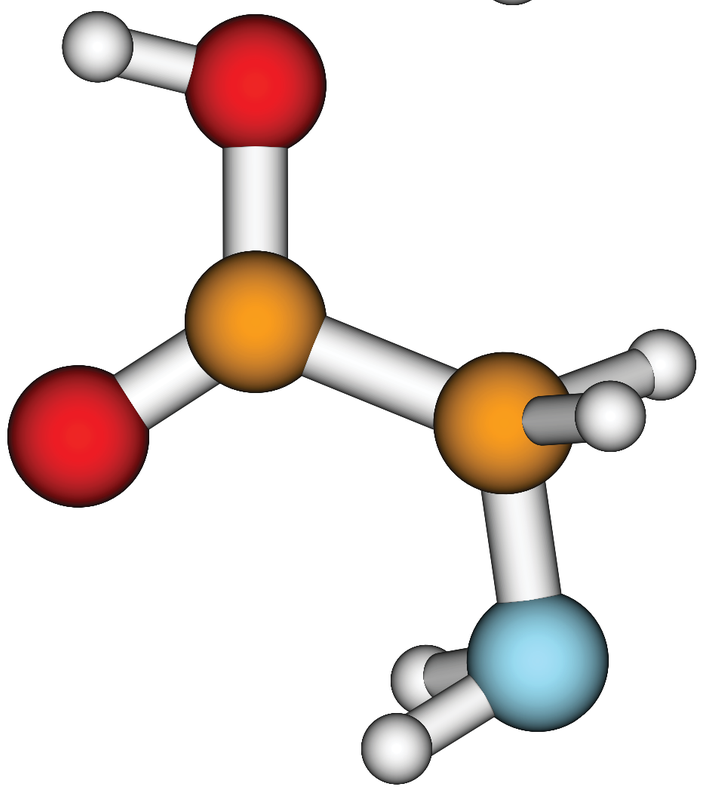
CoMotion

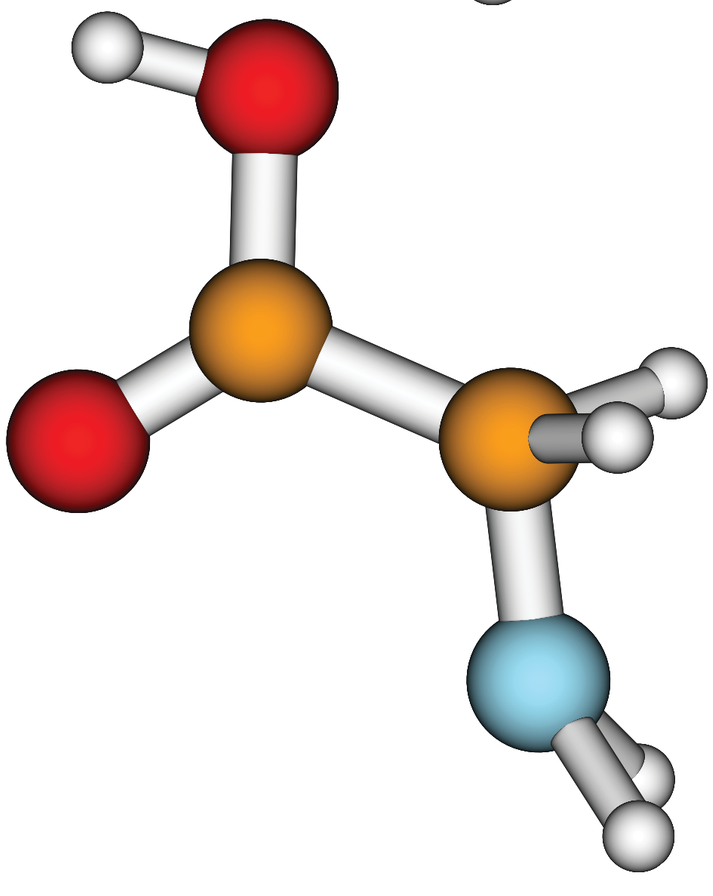
We are looking for motivated colleagues – please see https://www.controlled-molecule-imaging.org/careers

Physics and Chemistry of *complex* molecules
Structural isomers – conformers – of Glycine







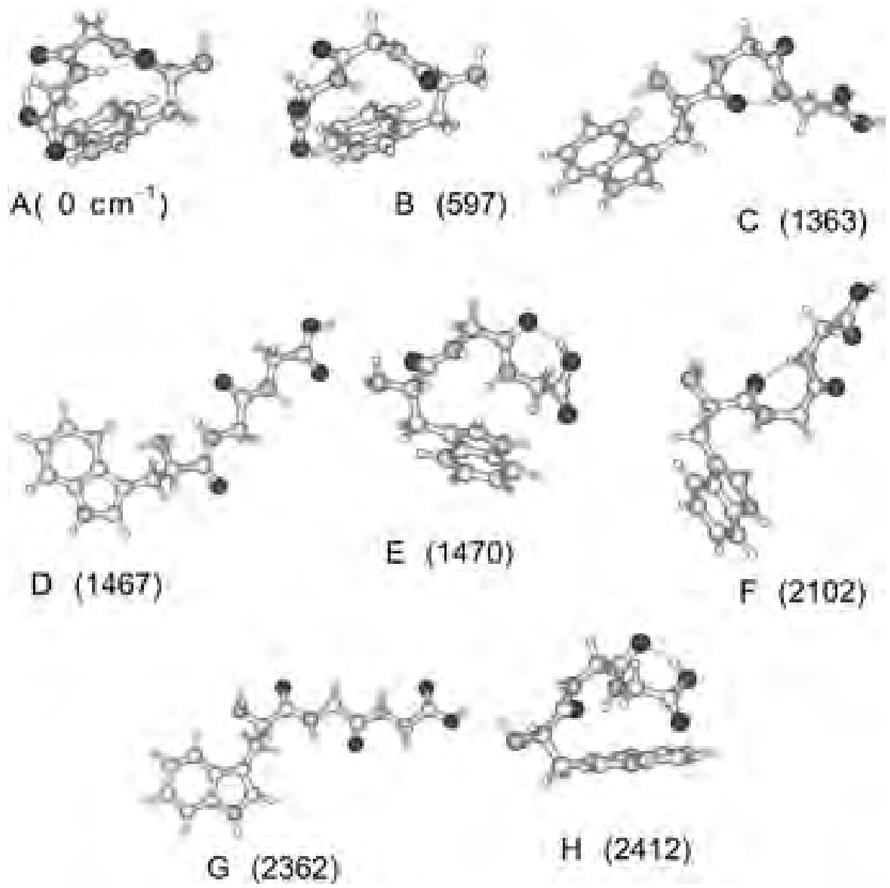


Complexity of molecules – “few body” quantum systems
Potential energy landscapes of isolated “floppy” molecules

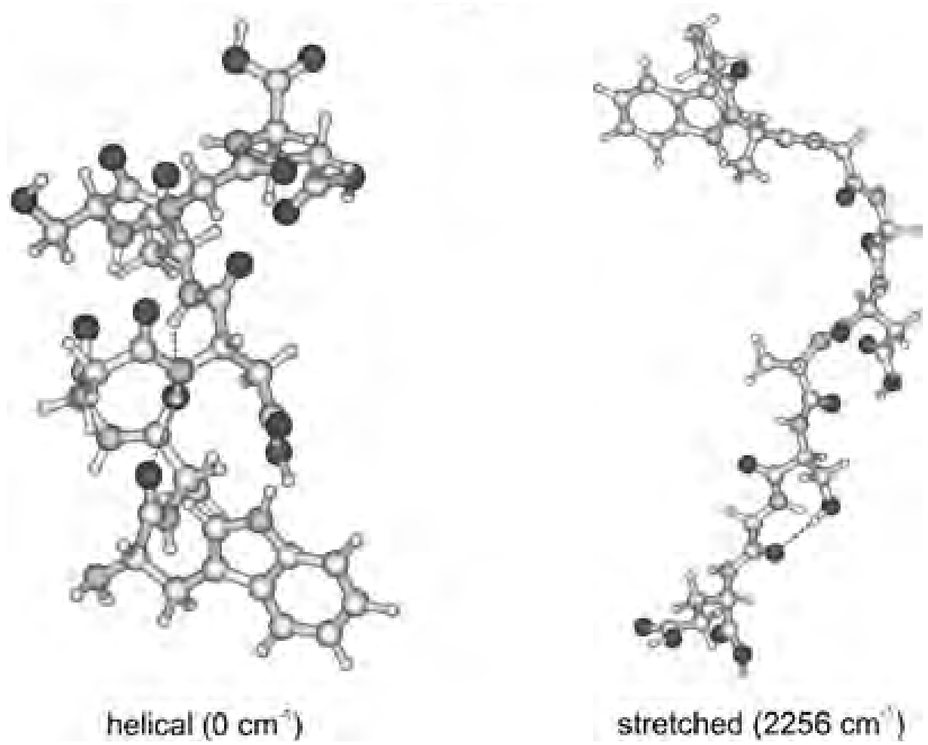
Exceptional points on the
phenylalanine potential energy hypersurface

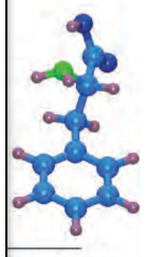
and bigger…
intra-molecular interactions become dominant

Trp-Gly-Gly



Delta sleep-inducing peptide
(Trp-Ala-Gly-Gly-Asp-Ala-Ser-Gly-Glu)



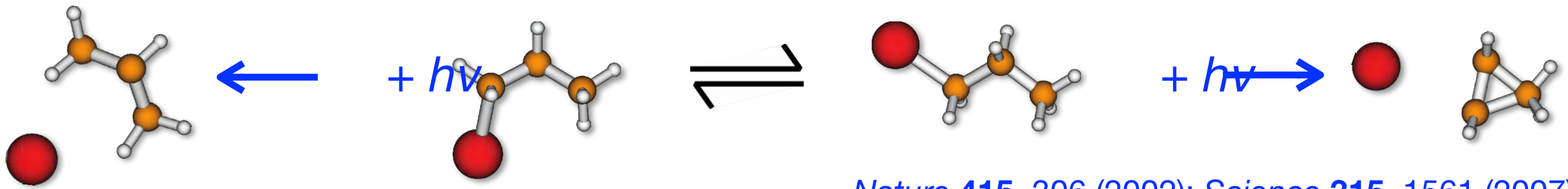


1 cm^{-1} ≙ 30 GHz ≙ 12 J/mol ≙ 0.12 meV ≙ 4.6 μHartree ≙ 1.4 K

Physics and Chemistry of complex molecules
Unraveling the structure-function relationship

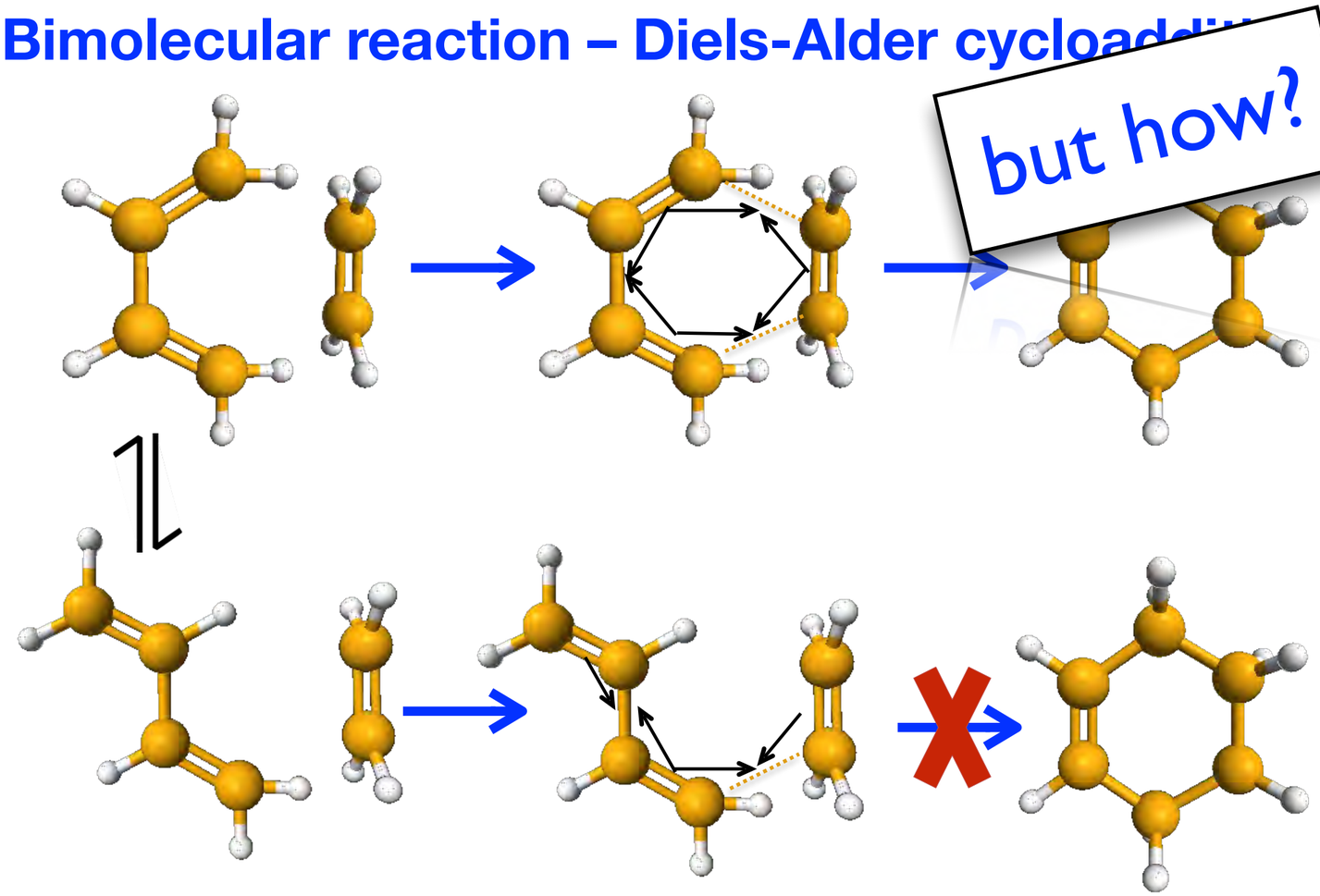
"Structure determines function"

Photodissociation of iodopropane



Nature **415**, 306 (2002); *Science* **315**, 1561 (2007)

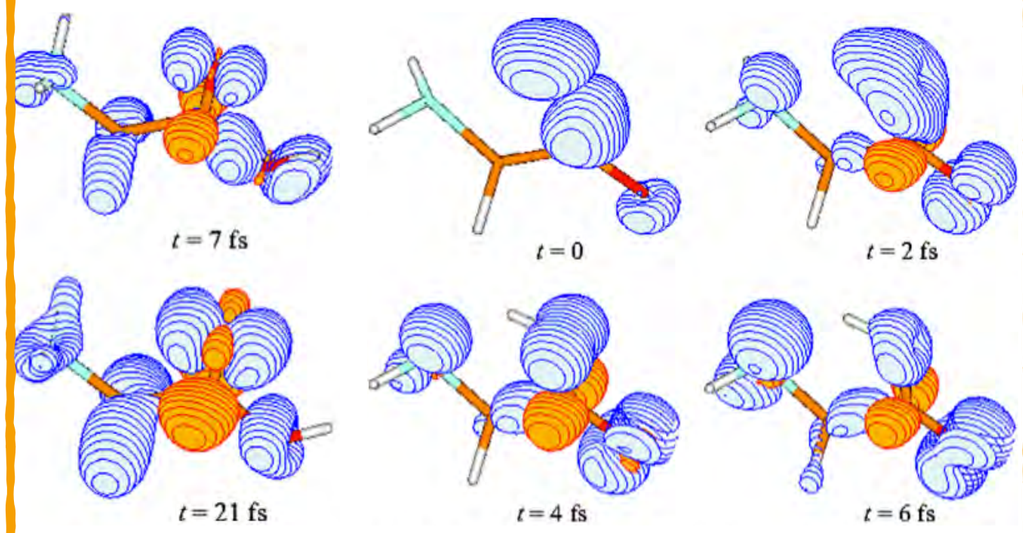
Bimolecular reaction – Diels-Alder cycloadd



Angew. Chem. Int. Ed. **19**, 779 (1980)

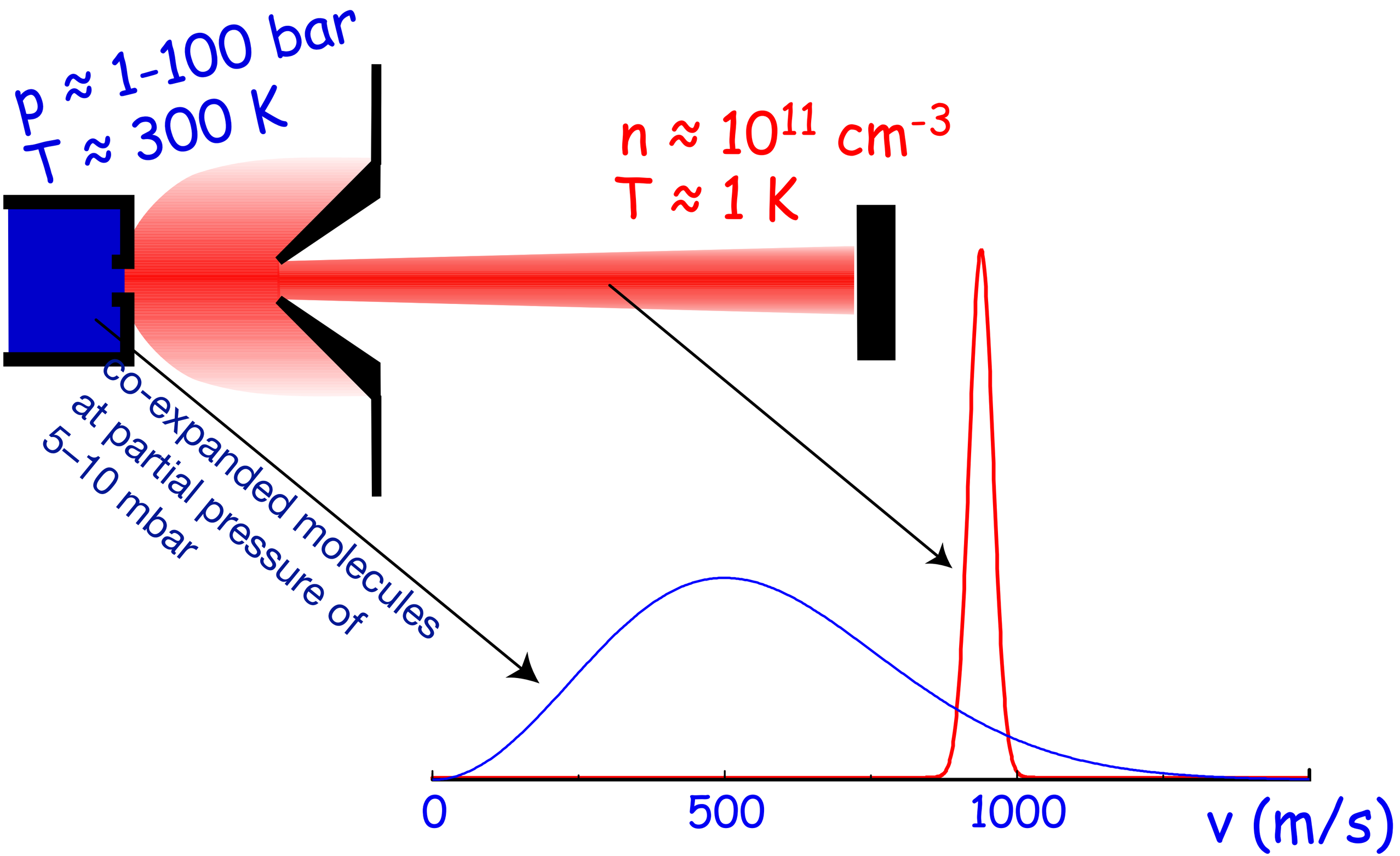
arge (electron hole) migration

21 fs Glycine II – 6 fs



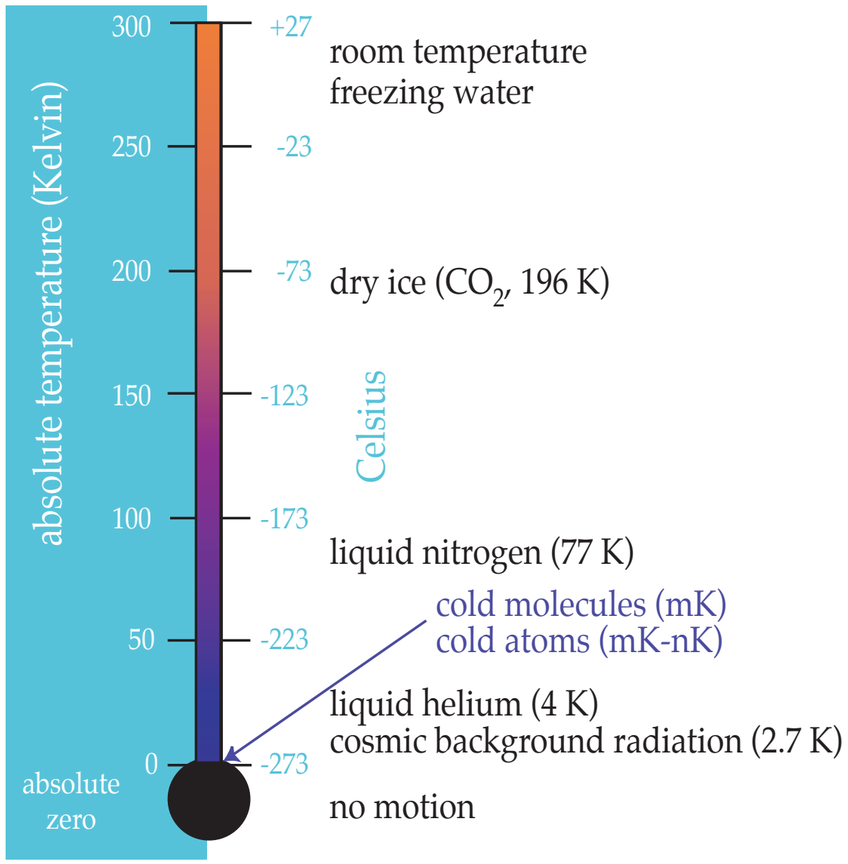
uleff, Cederbaum, *Chem. Phys*. **338**, 321 (2007)

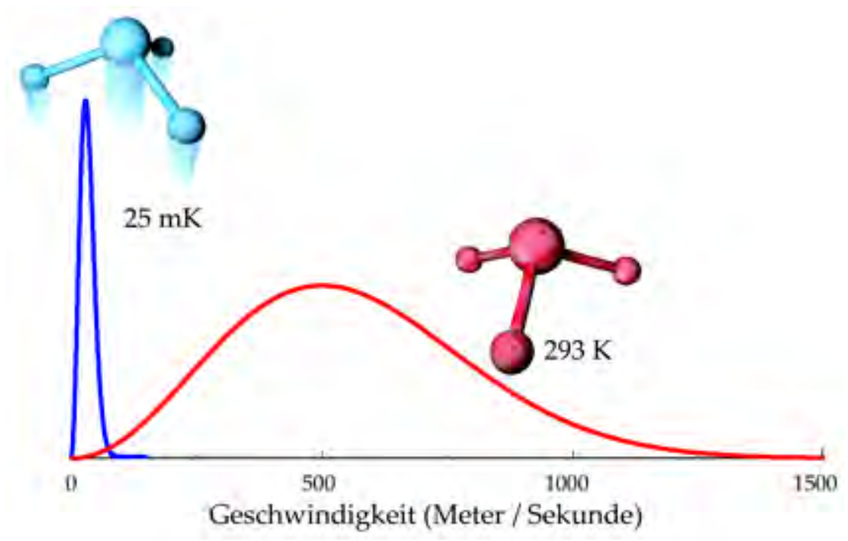
Manipulating the motion of neutral molecules
Production of controlled/cold molecular samples



Cold and Controlled Molecules – when are molecules cold?

Cold matter is slow – fairly controlled – matter





- Temperature T characterizes the velocity distribution of atoms/molecules.
  Under *normal* conditions ($T = 300\,\mathrm{K}, p = 1\,\mathrm{bar}$):
  $\bar{v} = 500\,\mathrm{m/s}$.
- A velocity distribution with a width of $5\,\mathrm{m/s}$, corresponds to $T = 30\,\mathrm{mK}$.
- Cold Molecules are slow molecules, "kinematically challenged"

When are molecules cold?

Internal degrees of freedom

- Molecules have various internal degrees of freedom:
  electronic, vibrational, rotational, nuclear spin, ...
- All these degrees of freedom are quantized!
- Orientation of molecules in external fields is also quantized!

Definition: Cold Molecules

Cold Molecules are *translationally* and *internally* cold:

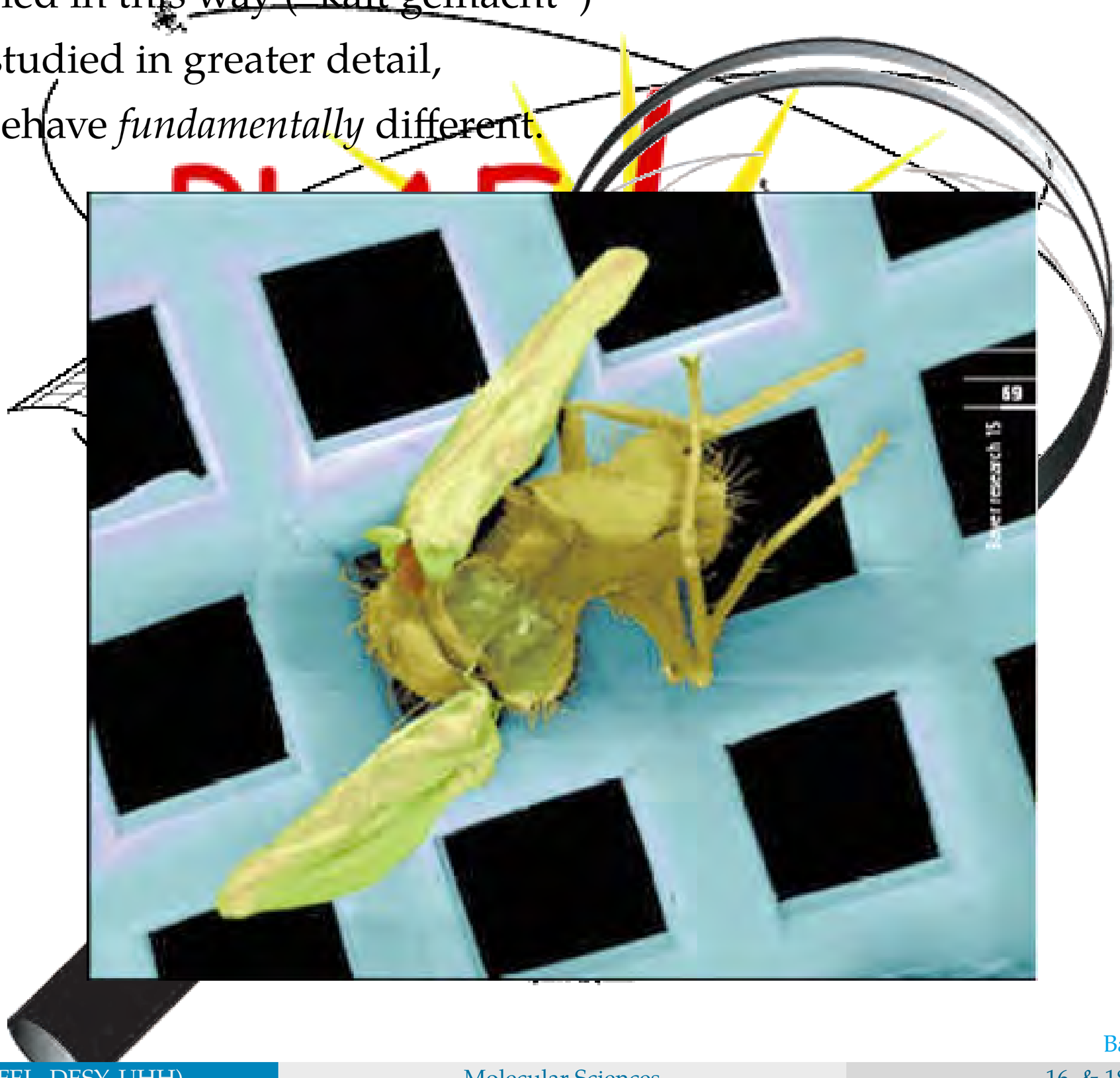
- they move slowly
- they are in a few, or even a single (rotational, vibrational, . . .) quantum-state(s), preferably (but not necessarily) in the absolute ground-state.

Additionally, the molecules shall be oriented in space.

Cold matter behaves differently

Matter handled in this way (“kalt gemacht”)

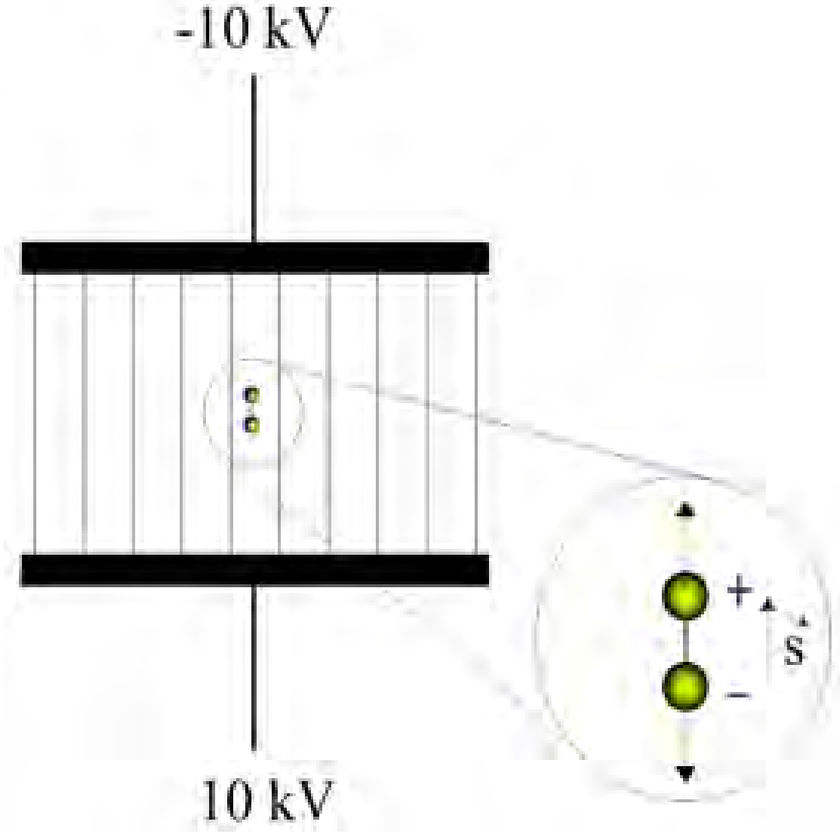
- can be studied in greater detail,
- might behave *fundamentally* different.

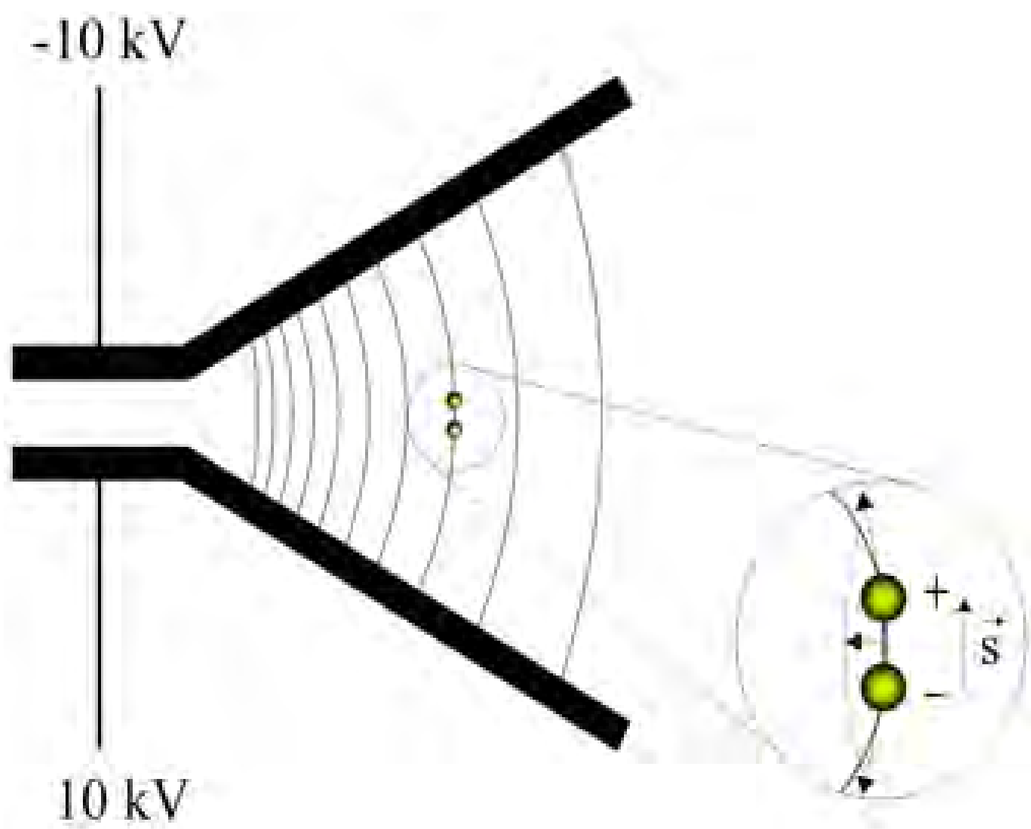


Bayer *Research* **15**, 64 (2004)

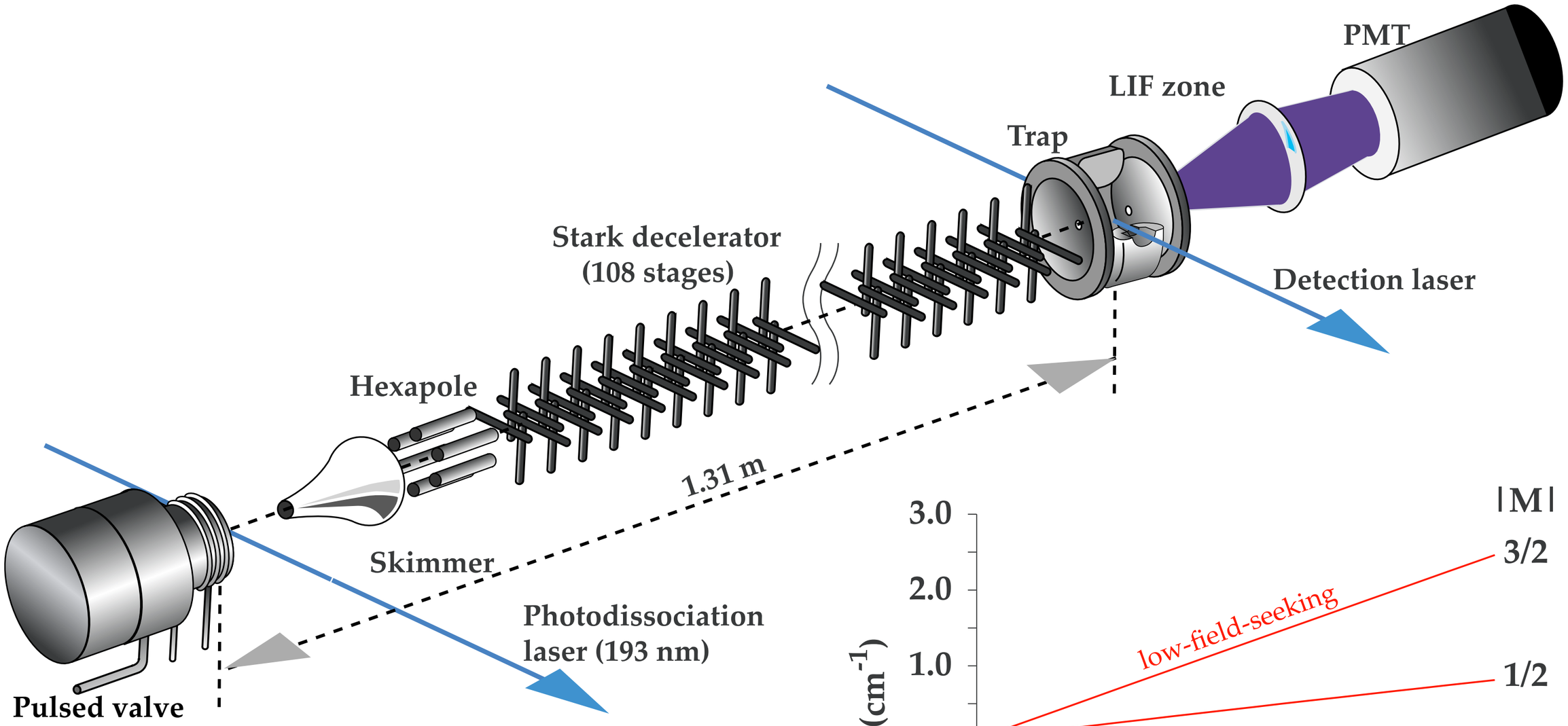
How can we control the velocity of neutral molecules?

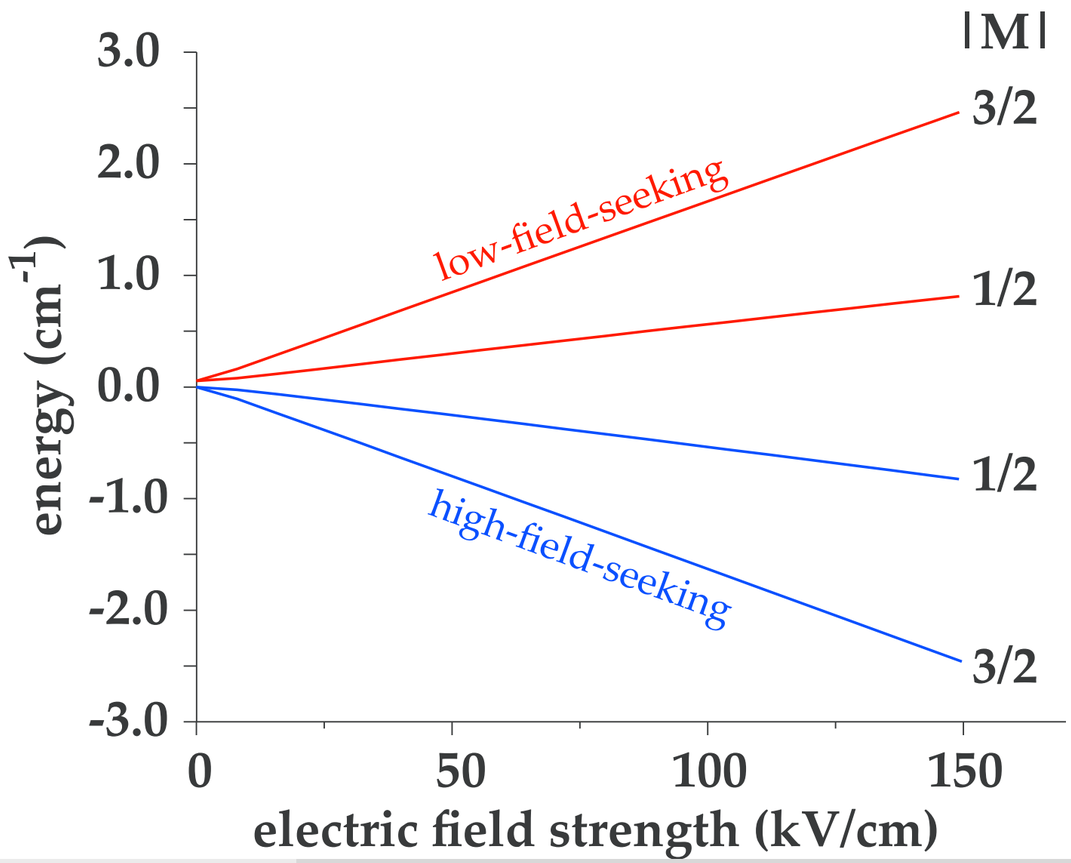
Force on a polar molecule in an (in)homogeneous electric field:



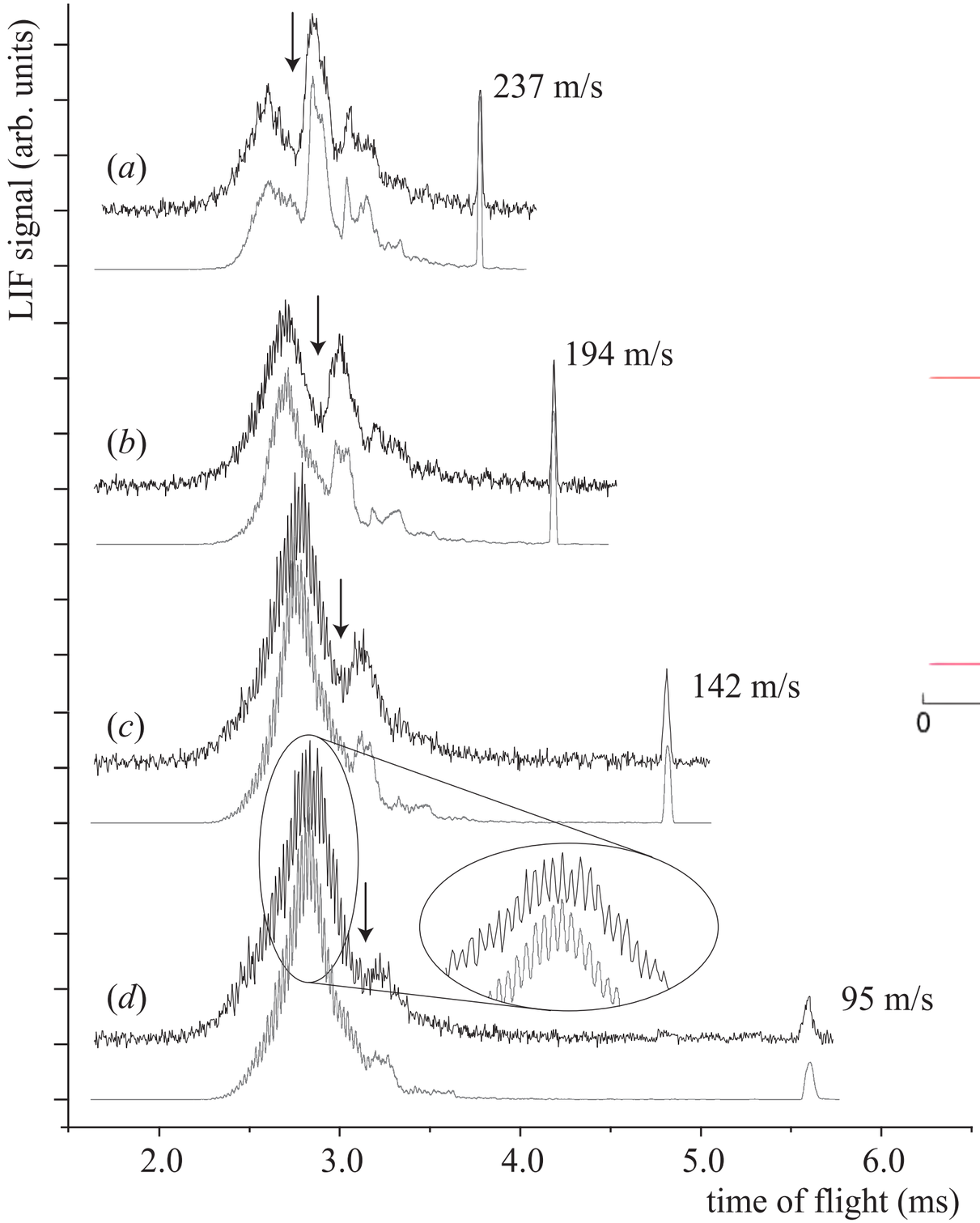


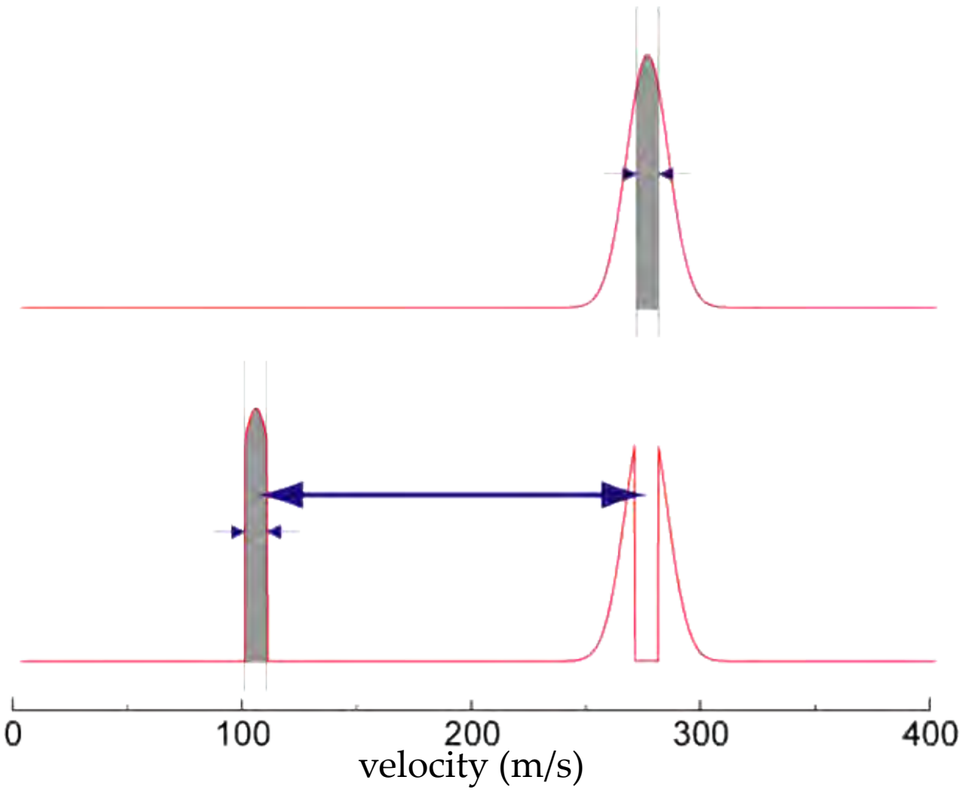
Experimental setup of the Stark decelerator





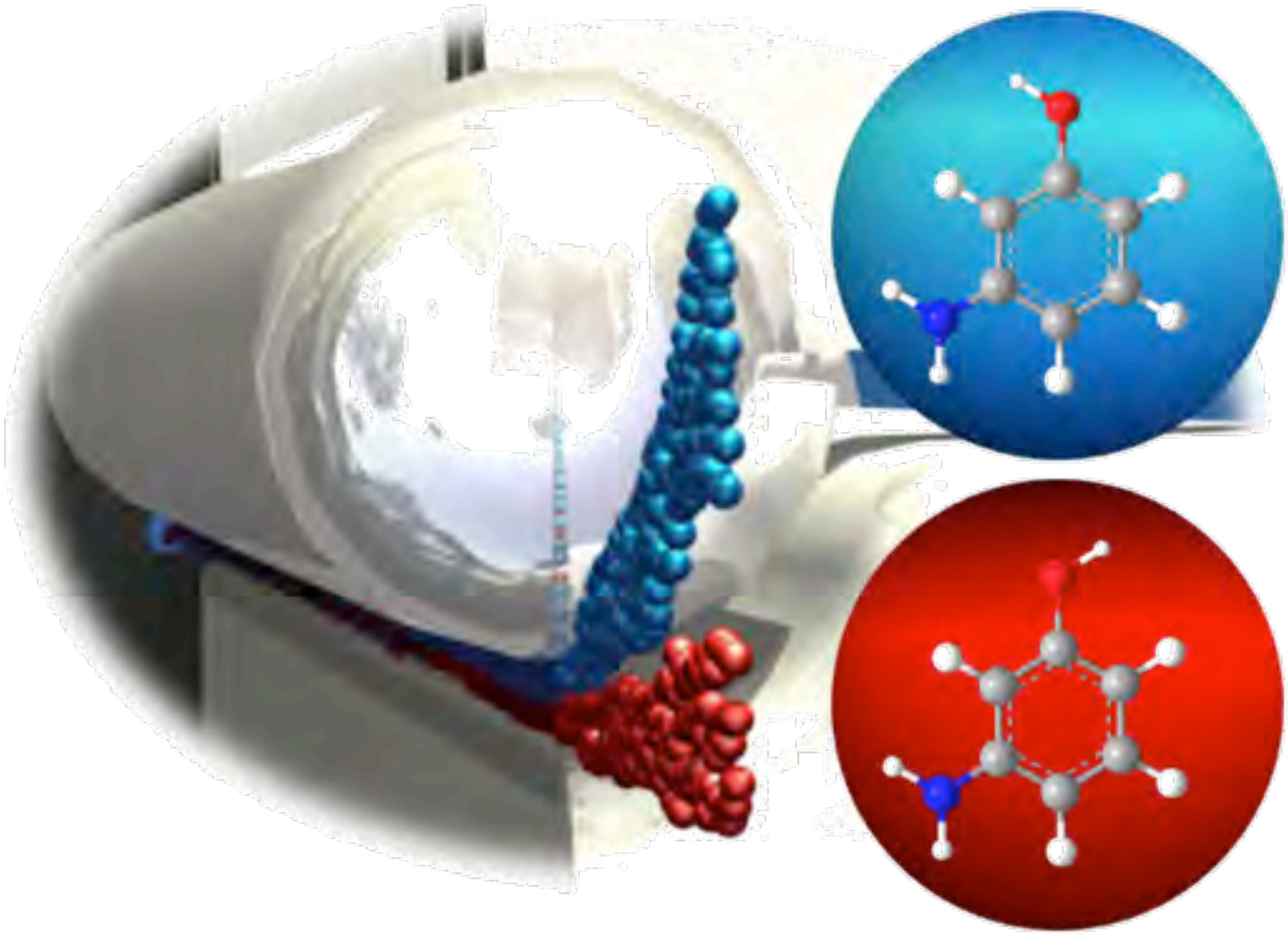
Decelerating OH ($X\,^2\Pi_{3/2}$, $v = 0$, $J = {}^3/_2$)





The electric deflector

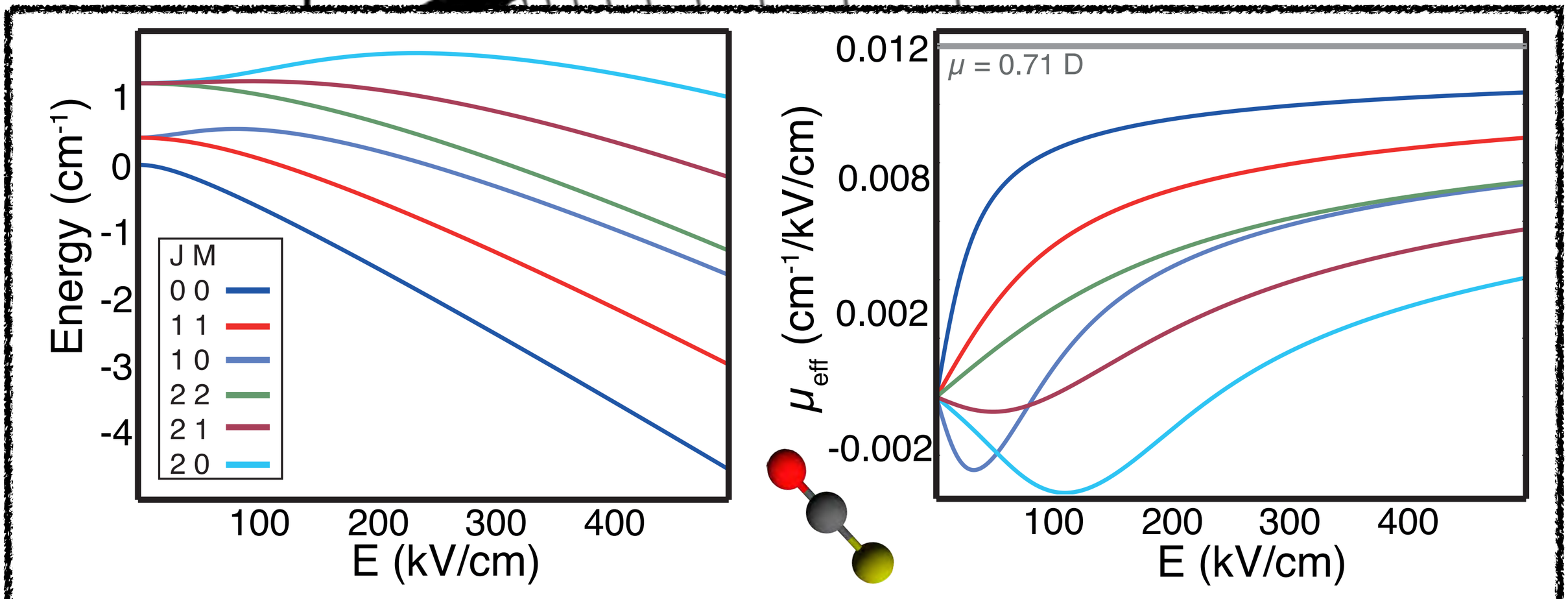
Quantum-state selection for complex molecules (but no speed change)



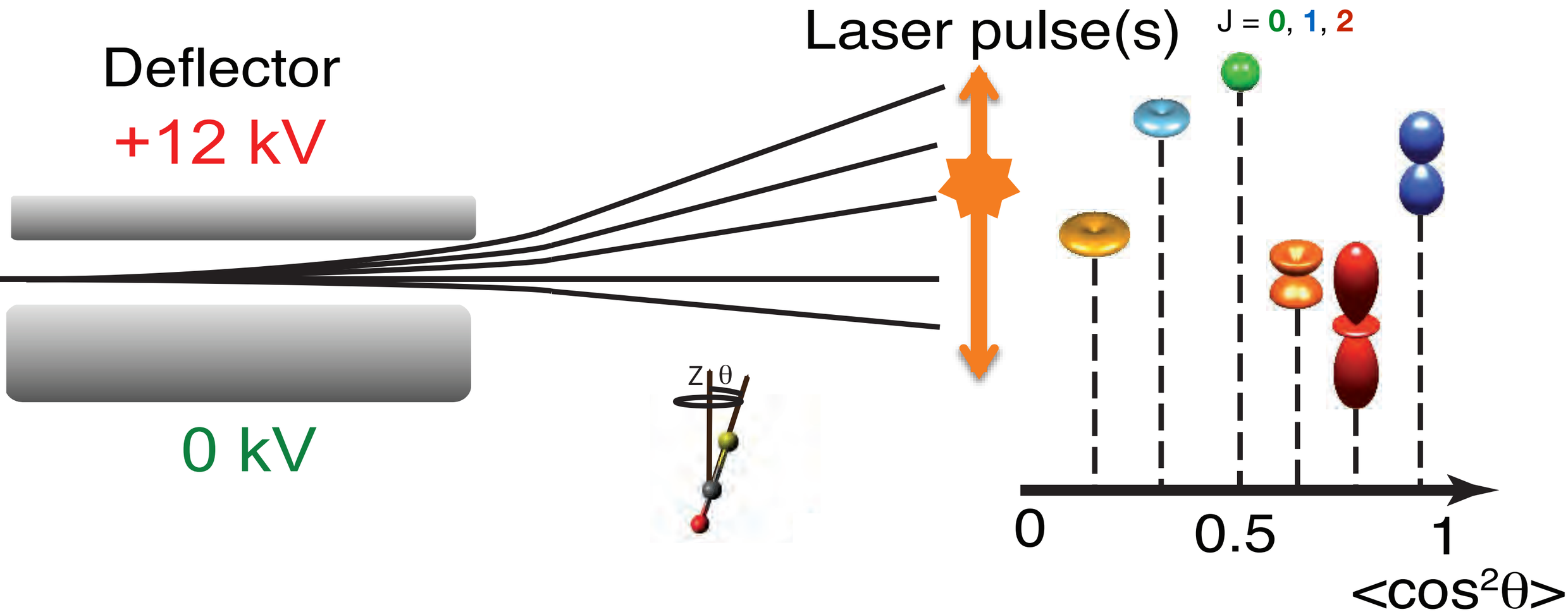
Chang, Horke, Trippel, Küpper, *Int. Rev. Phys. Chem.* **34**, 557 (2015)

Interactions of molecules with electric fields

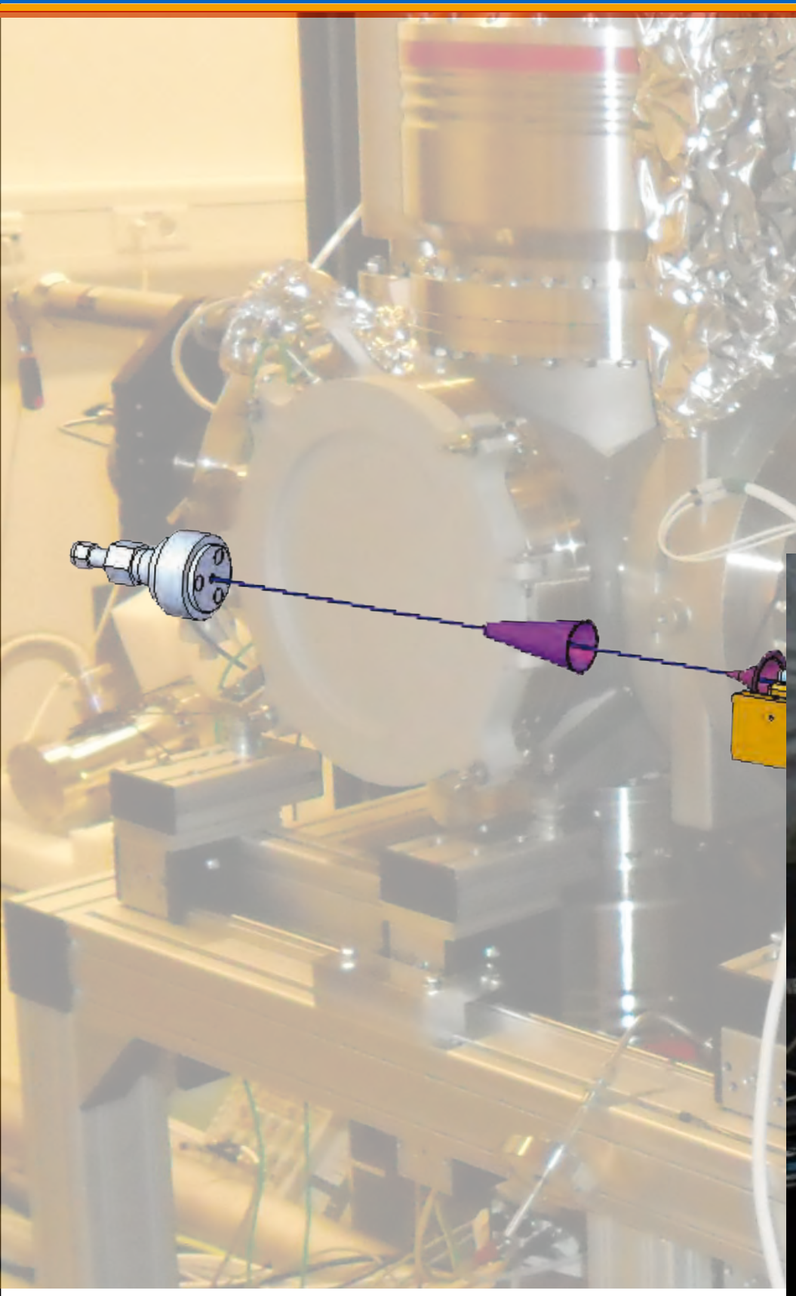
In “quantum-mechanical” reality, the Stark effect (the laboratory-fixed dipole moment) depends on the exact quantum state,

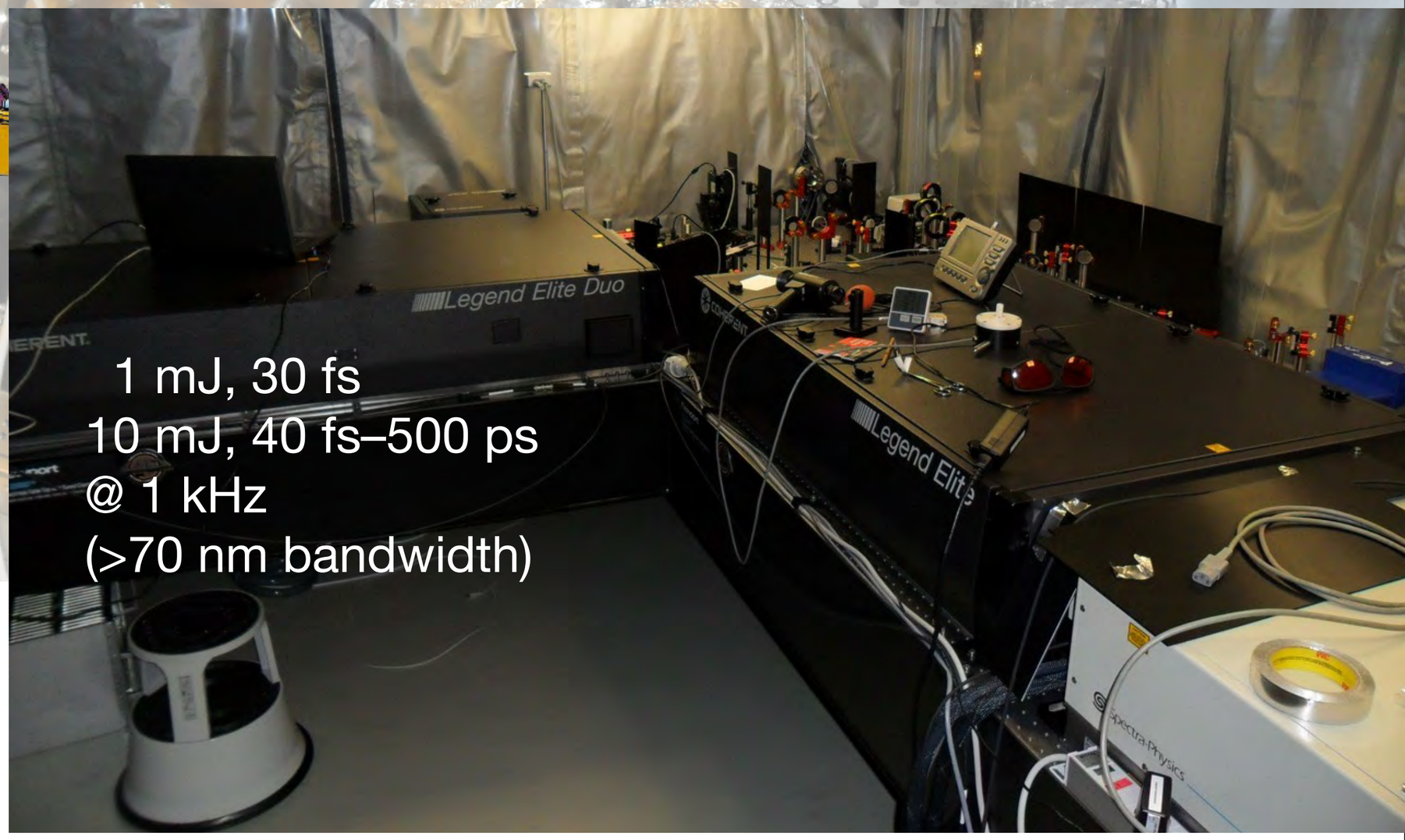


Dispersion of molecules by an electric field



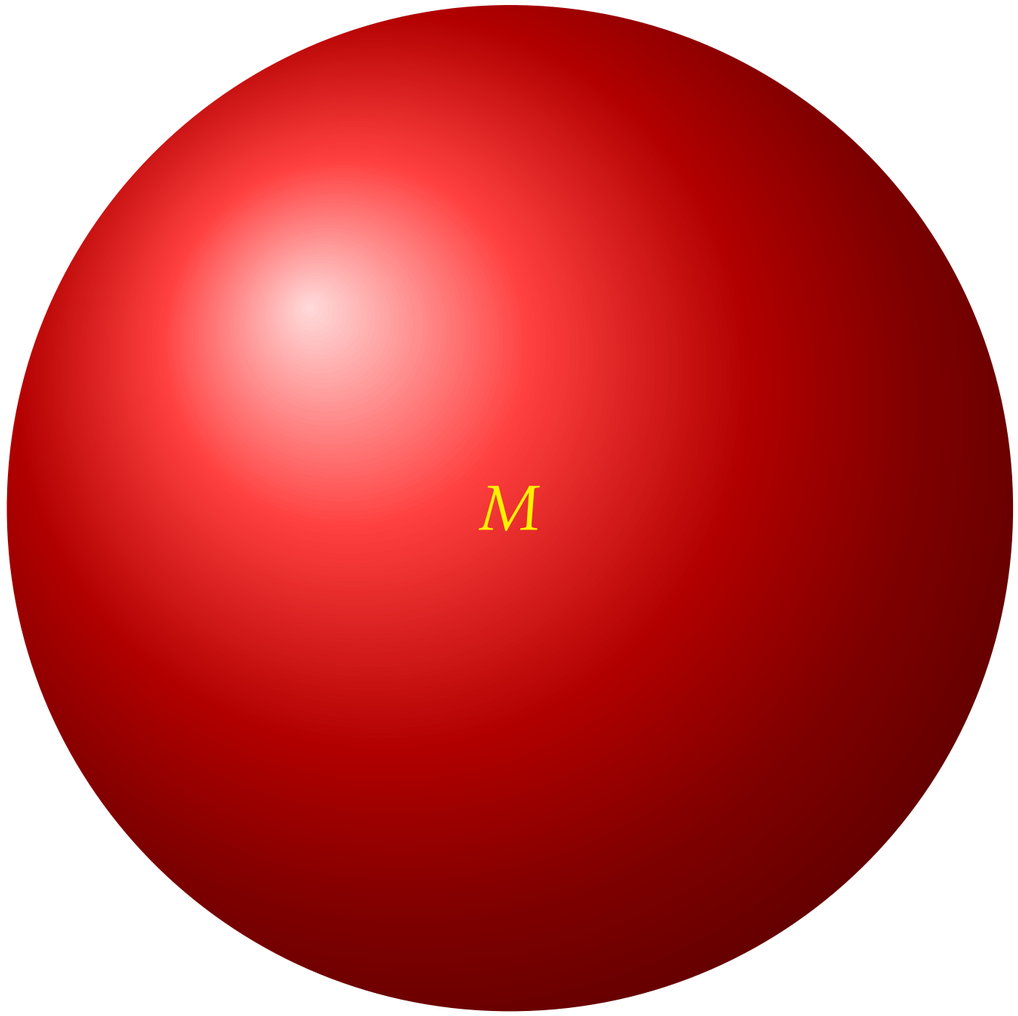
Toward time-resolved imaging of chemical dynamics kHz-rate manipulation experiments

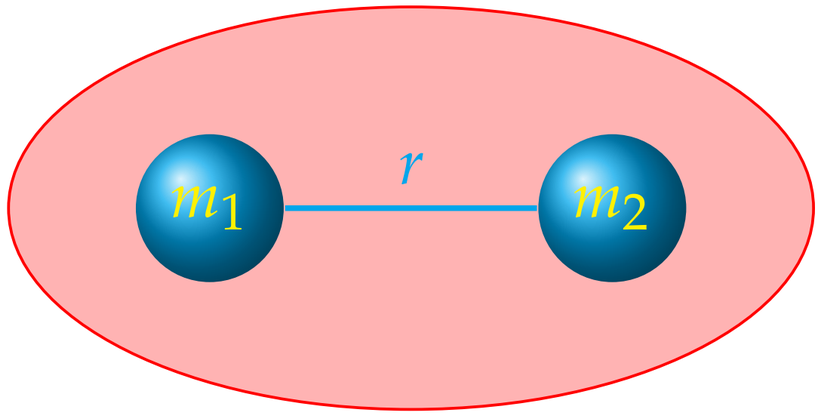




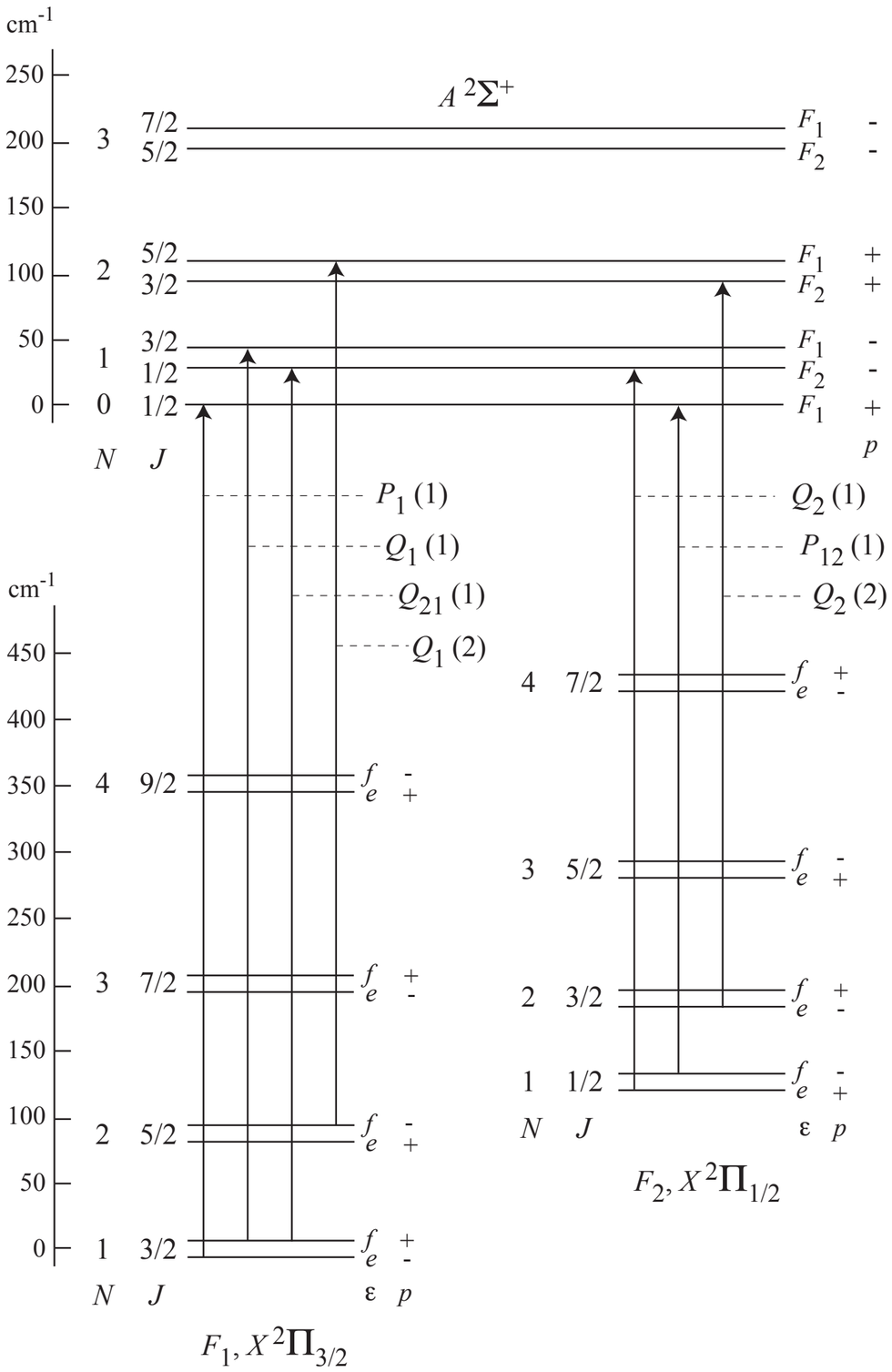
1 mJ, 30 fs
10 mJ, 40 fs–500 ps
@ 1 kHz
(>70 nm bandwidth)

(Diatomic) molecules





Term scheme of OH (radical)

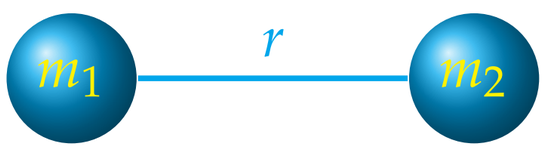


- Distinct quantum states due to
  - electronic,
  - vibrational,
  - rotational,
  - ...

  degrees of freedom
- We will now derive all these quantum numbers. . .

Molecule
A set of atoms

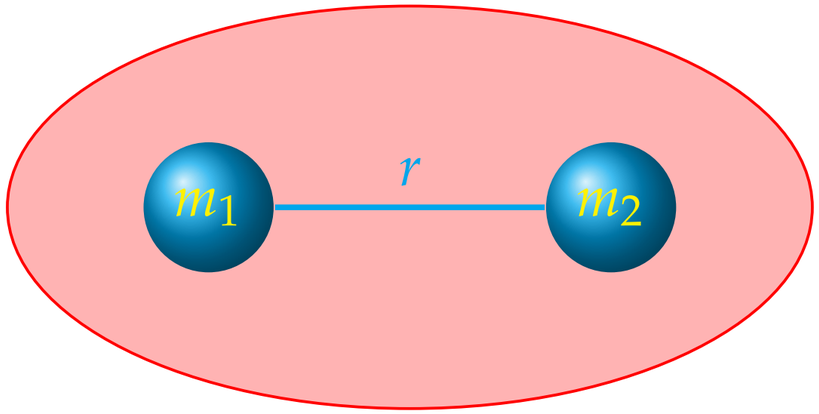
- Example: diatomic molecule:
  - Dumb-bell model: two point masses (m_1, m_2) separated by r.



- Semi-rigid nuclear frame immersed in the charge cloud of the molecular electrons.
- homo-nuclear — all atoms identical
  hetero-nuclear — different atoms present

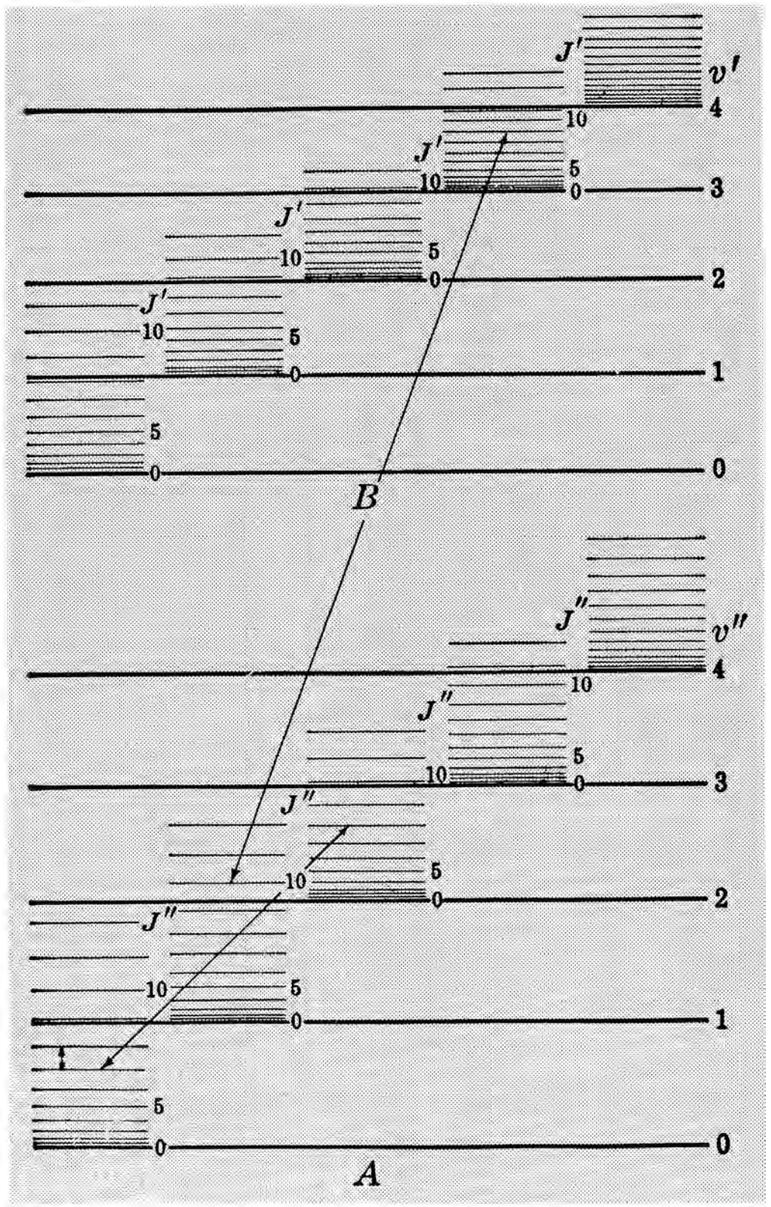
Molecule
A set of atoms

- Example: diatomic molecule:
  - Dumb-bell model: two point masses (m_1, m_2) separated by r.



- Semi-rigid nuclear frame immersed in the charge cloud of the molecular electrons.
- homo-nuclear — all atoms identical
  hetero-nuclear — different atoms present

Energy scale

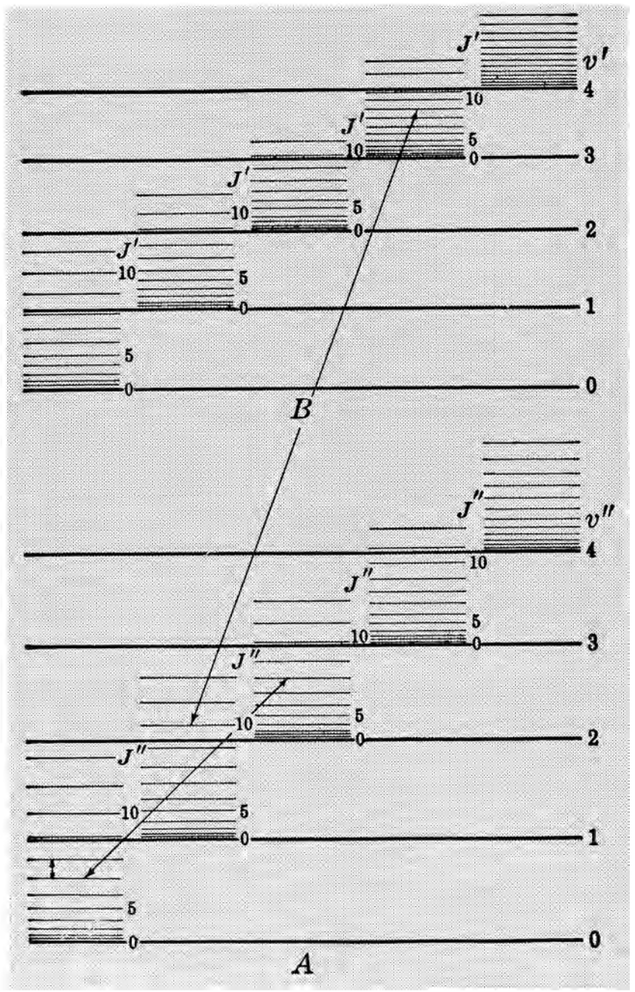


- Energy-scale of electronic states: 10000–50000 cm^{-1}
- Energy-scale of vibrational states: 100–4000 cm^{-1}
- Energy-scale of rotational states: 1–20 cm^{-1}
  (for larger molecules down to 1 GHz or less)
- Molecules *perform* all motions at the same time.
- Within one rotational period molecules typically vibrate 10-100 times.

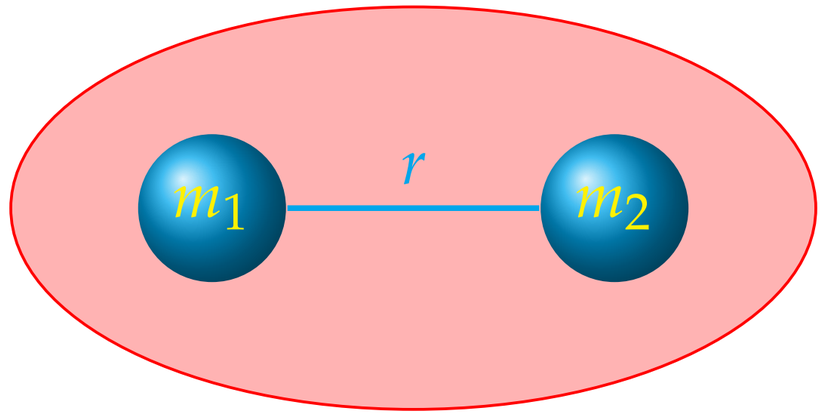
$$1\,\mathrm{eV} = 8065.5\,\mathrm{cm}^{-1} = 241.799\,\mathrm{THz} = 96.5\,\mathrm{kJ/mol} \quad (1)$$

See also the OH term scheme.

Born-Oppenheimer approximation



- Separation of electronic and nuclear motion:
  - Energy-scale of electronic states: 10000–50000 cm^{-1}
  - Energy-scale of vibrational states: 100–4000 cm^{-1}
  - Energy-scale of rotational states: 1–20 cm^{-1}
    (for larger molecules down to 1 GHz or less)
- Molecules *perform* all motions at the same time.



- Seen from the electrons, the nuclear frame is rigid in space.
- The slowly moving nuclei see a smeared out electronic charge cloud (whose effect on the nuclei depends on the internuclear separation).
  Or: the electrons adjust, essentially instantaneously, to the changing position of the nuclei.

Born-Oppenheimer approximation

Separation of electronic and nuclear motion

Definition: Born-Oppenheimer approximation

Electrons are lighter and faster than the nuclei. For the electrons the nuclei seem to be fixed in space, and the nuclei move in an effective distribution of electrons (electron cloud).

- The molecular wavefunction can be written as a product of a *nuclear* wavefunction and an *electronic* wavefunction, where the nuclear coordinates $\vec{R}_j$ are parameters:

$$\Psi\left(\vec{r}_i, \vec{R}_j\right) = \Psi_{\mathrm{e}}\left(\vec{r}_i; \vec{R}_j\right) \cdot \Psi_{\mathrm{n}}\left(\vec{R}_j\right) \tag{2}$$

- The eigenvalues of the electronic wave equation serve as an *effective potential* for the nuclear motion in the vicinity of the field configuration $\vec{R}_j$.
- Electrons move as if the nuclei were fixed in their instantaneous positions and follow the nuclear motion adiabatically.
- Electrons do not make transitions to other states, the electronic states are only deformed by the nuclear displacements.
- The electronic isotope shift is zero within the Born-Oppenheimer approximation.

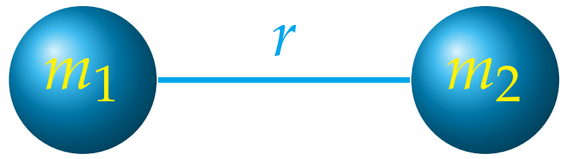
M. Born, R. Oppenheimer: Zur Quantentheorie der Molekeln. *Annalen der Physik* **389**, 457–484 (1927)

Separation of rotational and vibrational motion

- Separation of translation: $3N-3$ coordinates in the center of mass frame. This separation is trivial in the absence of external fields.
- Separation of rotation: $3N-6$ ($3N-5$ for linear molecules) vibrational coordinates. But molecules are *not* rigid bodies, rotation and vibration are coupled! There are many ways to attach a "molecular frame", a set of axes that rotate with the molecule, to a non-rigid body — Eckart conditions, Eckart frame.
- The separated nuclear wavefunction reads in the end:

$$\Psi_{\mathrm{n}}\left(\vec{R}_j\right) = \Psi_{\mathrm{t}}\left(X_{\mathrm{cm}}, Y_{\mathrm{cm}}, Z_{\mathrm{cm}}\right) \cdot \Psi_{\mathrm{r}}\left(\alpha, \beta, \gamma\right) \cdot \Psi_{\mathrm{v}}\left(Q_1, \ldots, Q_{3N-6}\right) \cdot \qquad (3)$$

Rigid diatomic rotor



- classical energy:

$$E_r = \frac{1}{2} I \omega^2 \qquad \text{with } I = m_1 r_1^2 + m_2 r_2^2 \tag{8}$$

with the reduced mass $\mu = \frac{m_1 m_2}{m_1 + m_2}$ and bond length $r = r_1 + r_2$ one obtains

$$E_r = \frac{1}{2} \mu r^2 \omega^2 \tag{9}$$

with $L = I\omega$ this yields

$$E_r = \frac{L^2}{2I} \tag{10}$$

- quantum mechanical energy:

$$E_r = \frac{h^2}{8\pi^2 I} J(J+1) \tag{11}$$

  - E_r is inversely proportional to I
  - E_r scales with rotational quantum number as $J(J+1)$

Term values

In molecular spectroscopy term values are used for convenience:

$$F(J) = \frac{E_r}{hc} = BJ(J+1) \tag{12}$$

with the rotational constant

$$B = \frac{h}{8\pi^2 cI} = \frac{h}{8\pi^2 c\mu r^2} \tag{13}$$

Here we use cm^{-1}, often also Hz (MHz) are used.

Typical rotational constants of diatomic molecules are $20\,\mathrm{cm}^{-1}$ for hydrides (HF, OH, CH, ...) to less than $1\,\mathrm{cm}^{-1}$ for heavier small molecules; they become very small (e.g., $< 10^{-6}\ \mathrm{cm}^{-1}$) for large polyatomic molecules.

	$B_e\ (cm^{-1})$	$r_e\ (10^{-12}\ \mathrm{m})$
H_2	60.8	74.16
N_2	2.010	109.4
O_2	1.446	120.7
Li_2	0.673	267.3
NO	1.705	115.1
HCl	10.59	127.4

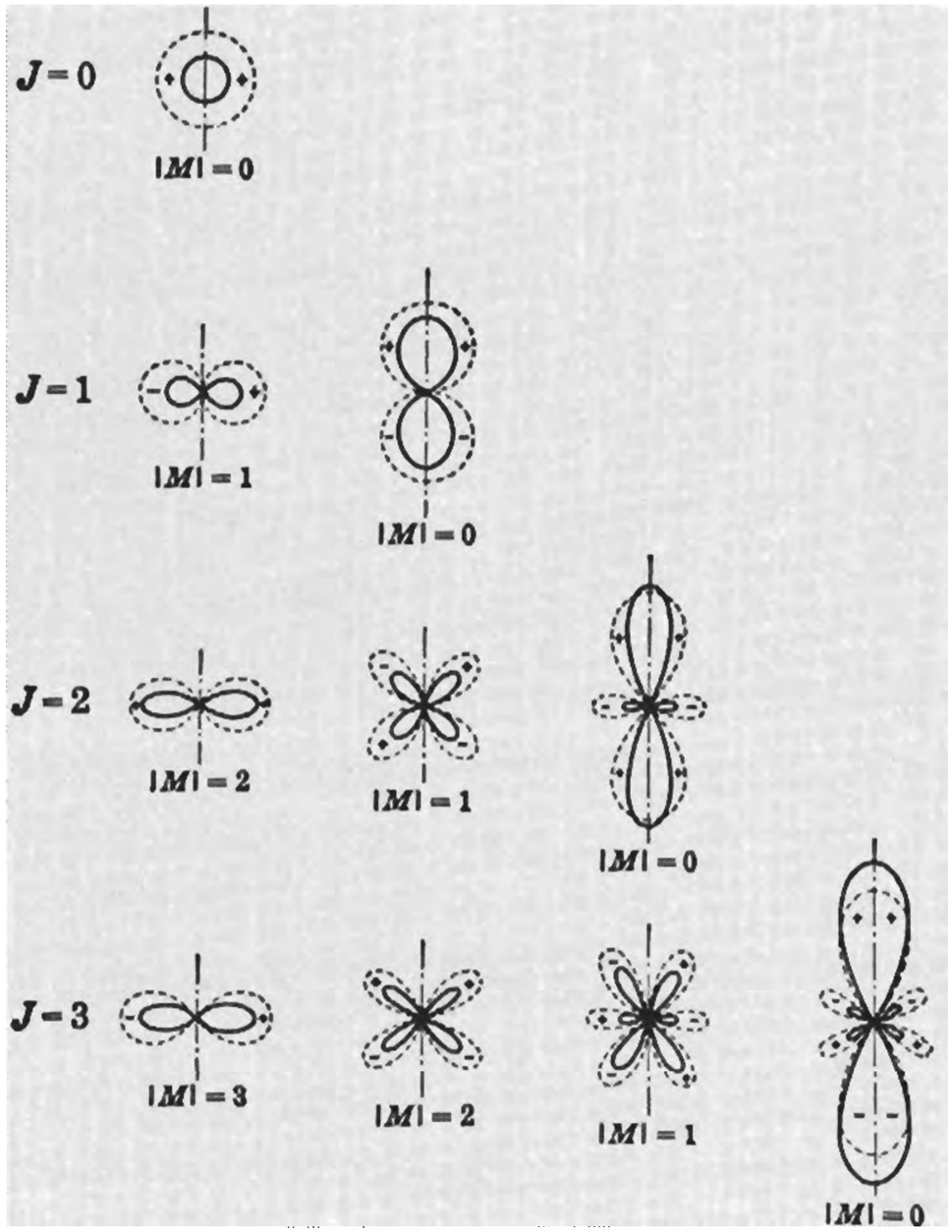
$$1\,\mathrm{cm}^{-1} \hat{=} 2.99 \cdot 10^{10}\,\mathrm{s}^{-1} \hat{=} 1.23992 \cdot 10^{-4}\,\mathrm{eV}$$

Rigid Rotor

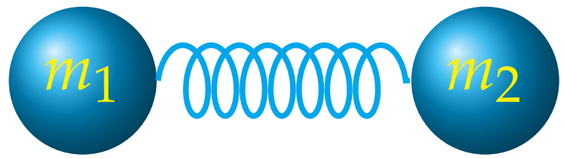
Wavefunctions and Probability Distributions

Wavefunctions of the rigid rotor are the spherical harmonics:

$$\Psi_{rot}(r) = Y_{JM}(\vartheta, \varphi) \tag{14}$$



Harmonic Oscillator



- Potential energy of harmonic oscillator:

$$V = \frac{1}{2}k(r - r_e)^2 \tag{15}$$

- Classical vibration frequency:

$$2\pi\nu_{\text{osc}} = \sqrt{\frac{k}{\mu}} \tag{16}$$

- Quantum-mechanical vibration energy:

$$E_{\text{vib}} = h\nu_{\text{osc}}(v + \frac{1}{2}) \tag{17}$$

  - energy levels are equidistant
  - ground state has finite (non-zero) energy

Harmonic Oscillator

- Term values in practically used units (cm^{-1}):

$$G(v) = \frac{E_{\mathrm{vib}}}{hc} = \omega_e (v + \frac{1}{2}) \tag{18}$$

with

$$\omega_e = \frac{\nu_{\mathrm{osc}}}{c} \tag{19}$$

- Example frequencies:

H_2	$4401\,\mathrm{cm}^{-1}$
HF	$4138\,\mathrm{cm}^{-1}$
OH	$3738\,\mathrm{cm}^{-1}$
HCl	$2991\,\mathrm{cm}^{-1}$
NaCl	$366\,\mathrm{cm}^{-1}$

http://webbook.nist.gov/chemistry/form-ser.html

Harmonic Oscillator

- Schroedinger equation:

$$\left[-\frac{\hbar^2\Delta}{2\mu}+\frac{k}{2}(r-r_e)^2\right]\Psi_{vib}(r-r_e)=E_{vib}\Psi_{vib}(r-r_e) \tag{20}$$

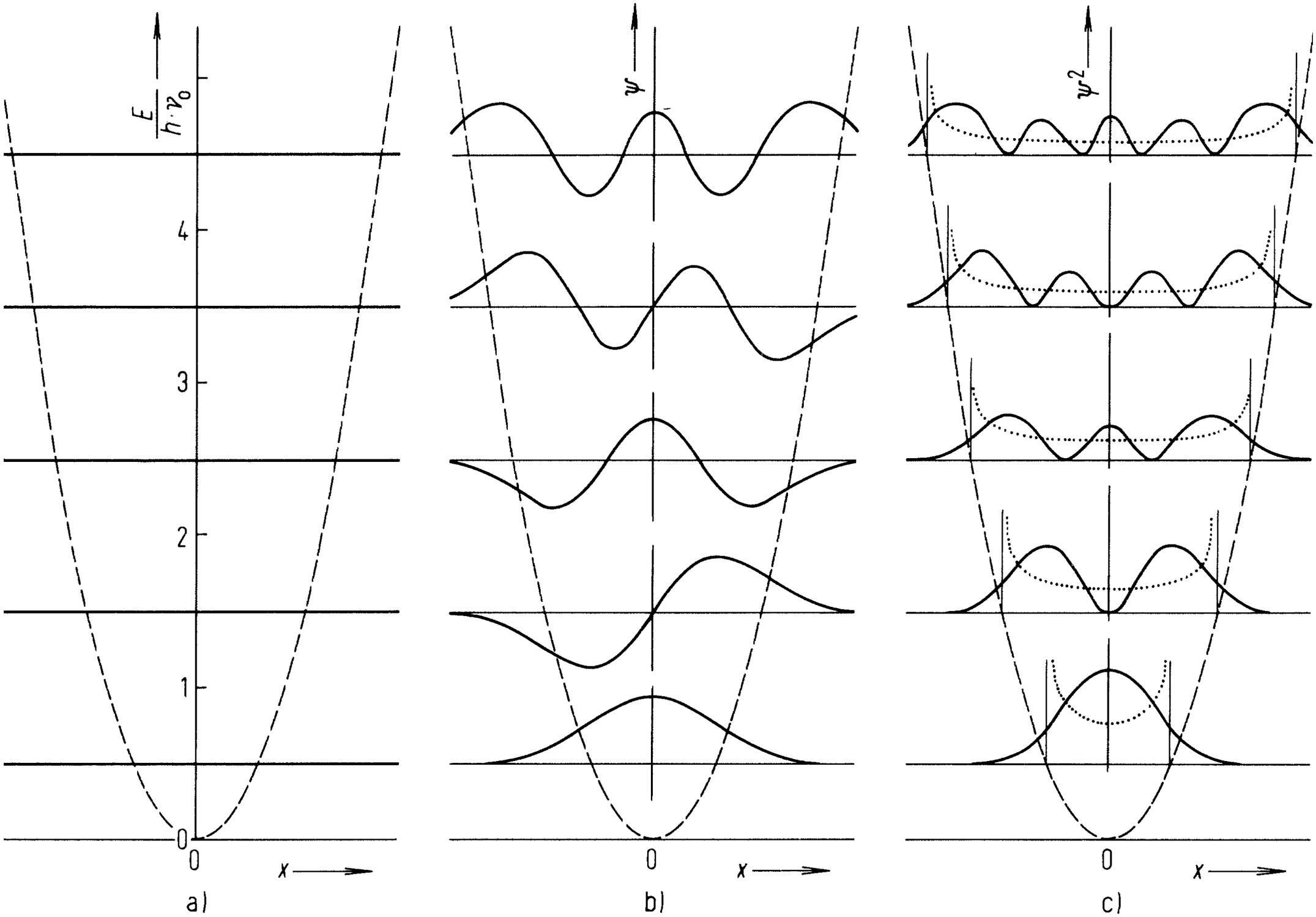
- Wavefunctions of the harmonic oscillator are the Hermite polynomials

v	E_v	Ψ
0	$\frac{1}{2}\hbar\omega_e$	$A_0\cdot e^{-\frac{\alpha}{2}(r-r_e)^2}$
1	$\frac{3}{2}\hbar\omega_e$	$A_1\cdot 2(r-r_e)\cdot e^{-\frac{\alpha}{2}(r-r_e)^2}$
2	$\frac{5}{2}\hbar\omega_e$	$A_2\cdot(1-2\alpha(r-r_e)^2)\cdot e^{-\frac{\alpha}{2}(r-r_e)^2}$

mit $\alpha=\frac{1}{\hbar}\sqrt{\mu\cdot k}$

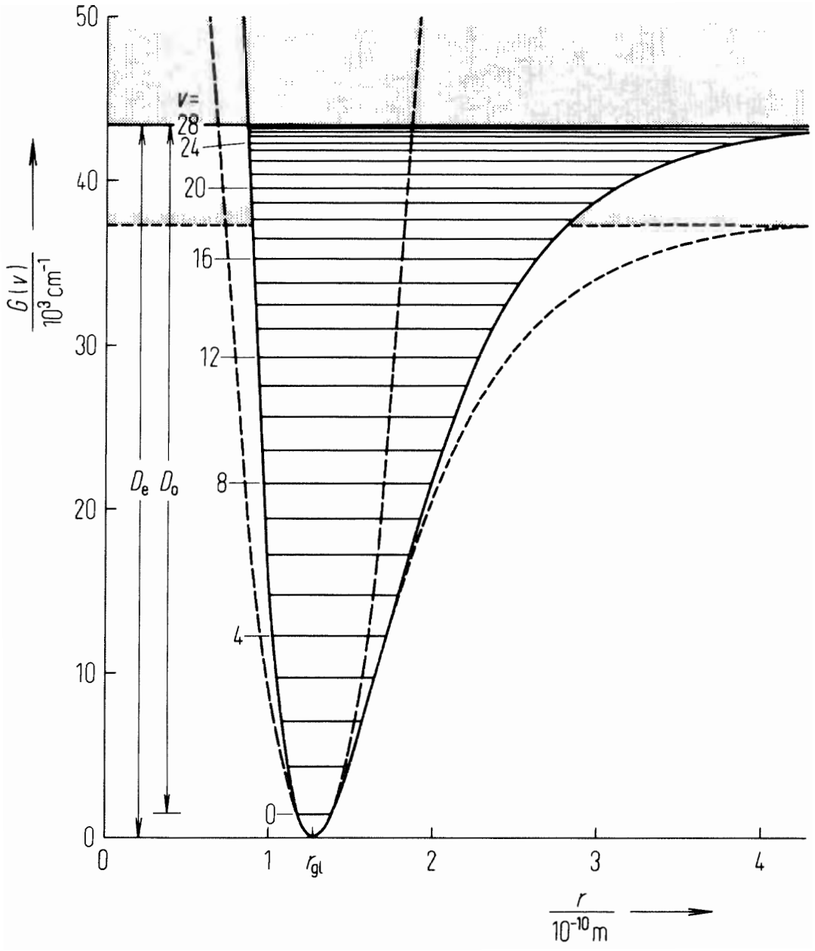
Harmonic Oscillator

Wavefunctions



Morse Oscillator

A more realistic potential must resemble the bond-breaking at large distance!



$$V = D_e \left(1 - e^{-\beta(r-r_e)}\right)^2 \quad (21)$$

- vibrational level spacing decreases
- finite number of vibrational levels (Compare Coulomb potential with an infinite number of bound states.)
- For small $r - r_e$:

$$V = D_e \left(1 - (1 - \beta(r - r_e))\right)^2 \quad (22)$$

- term values

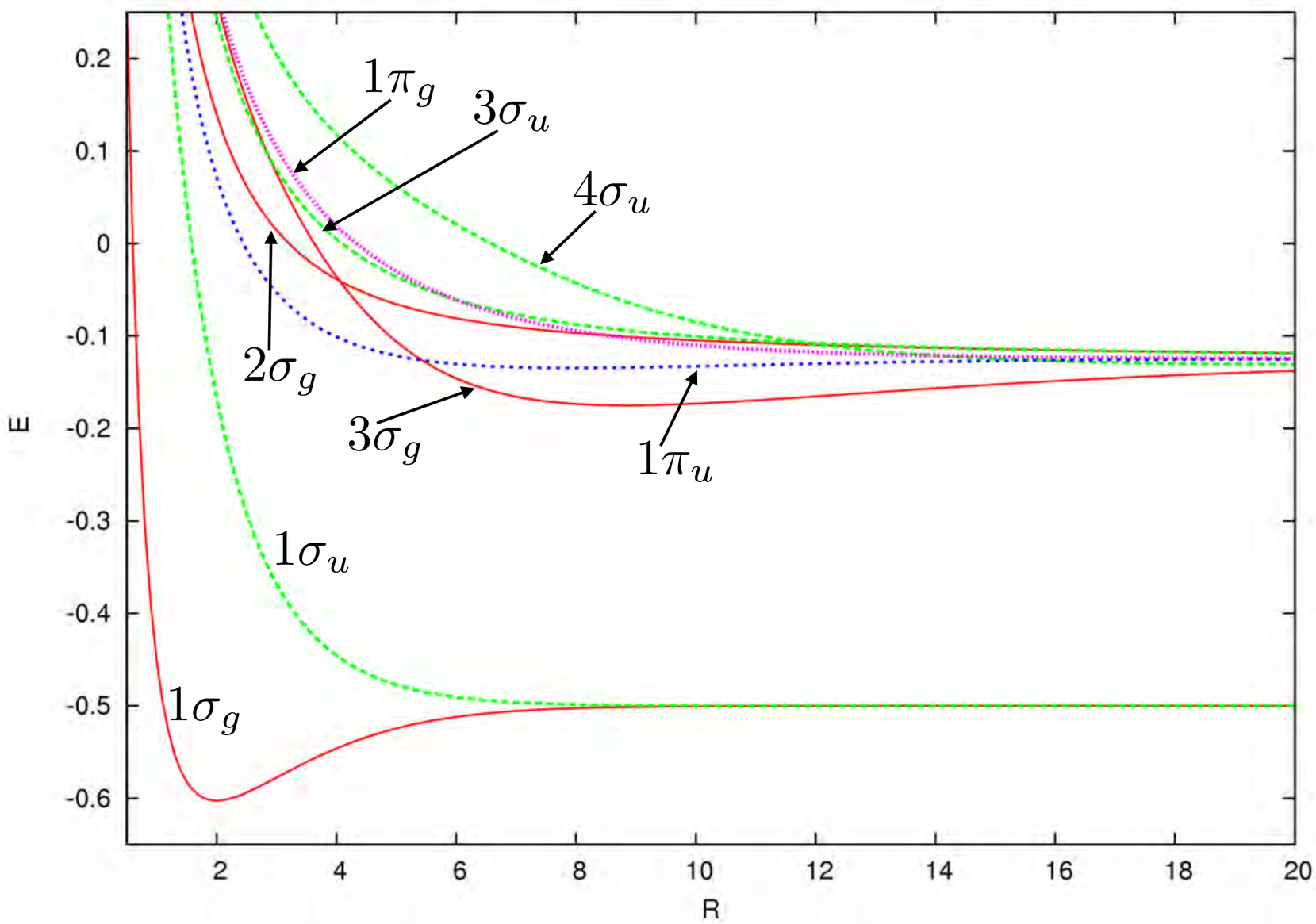
$$G(v) = \omega_e(v + \frac{1}{2}) + \text{correction term} \quad (23)$$

$$= \omega_e(v + \frac{1}{2}) - \omega_e x_e(v + \frac{1}{2})^2 + \omega_e y_e(v + \frac{1}{2})^3 \quad (24)$$

Potential energy surfaces

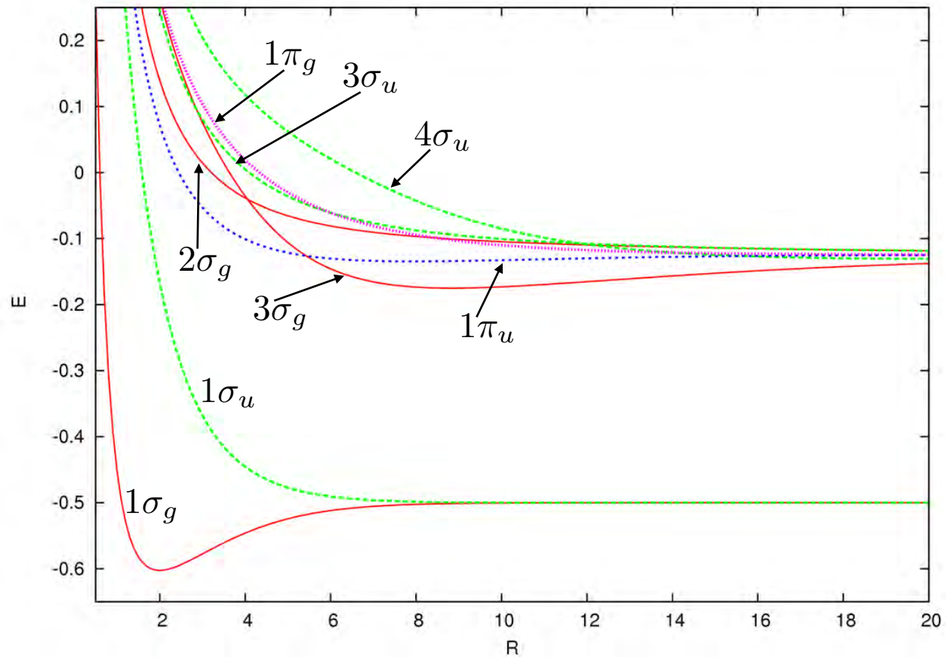
Electronic states of the simplest molecule: H_2^+

- *Effective potential* for the nuclear motion as a function of internuclear distance.
- Electrons do not make transitions to other states, the electronic states are only deformed by the nuclear displacements.



Symmetry classification of the electronic states

Electronic states of the simplest molecule: H_2^+



The states are labelled by two symmetry labels:

- Angular momentum projection on axis $\lambda = |m|$:

λ	0	1	2	3	4	...
	σ	π	δ	ϕ	γ	...

  The WF are eigenfunctions of $\hat{L}_z$

  $\Psi_e(z, r, \varphi) = F(z, r)(2\pi)^{-1/2} e^{im\varphi}$

- Parity: *gerade* (g) or *ungerade* (u)

  Which is possible because $[H_\mathrm{e}, \hat{L}_z] = 0$ and $[H_\mathrm{e}, \hat{\Pi}] = 0$ (where $\Pi\,\Psi(x_1, \ldots, x_f) = \Psi(-x_1, \ldots, -x_f)$ defines the parity operator)

Introduction to molecular terms for diatomics

Two electrons

Let's make a product *ansatz* for the wavefunction:

$$\Psi(1,2) = \psi^{(a)}_{m_1,(g,u)}(1)\psi^{(b)}_{m_2,(g,u)}(2) \tag{4}$$

- Angular momentum projection on axis $\Lambda = |m_1 + m_2|$:

Λ	0	1	2	3	4	...
	Σ	Π	Δ	Φ	Γ	...

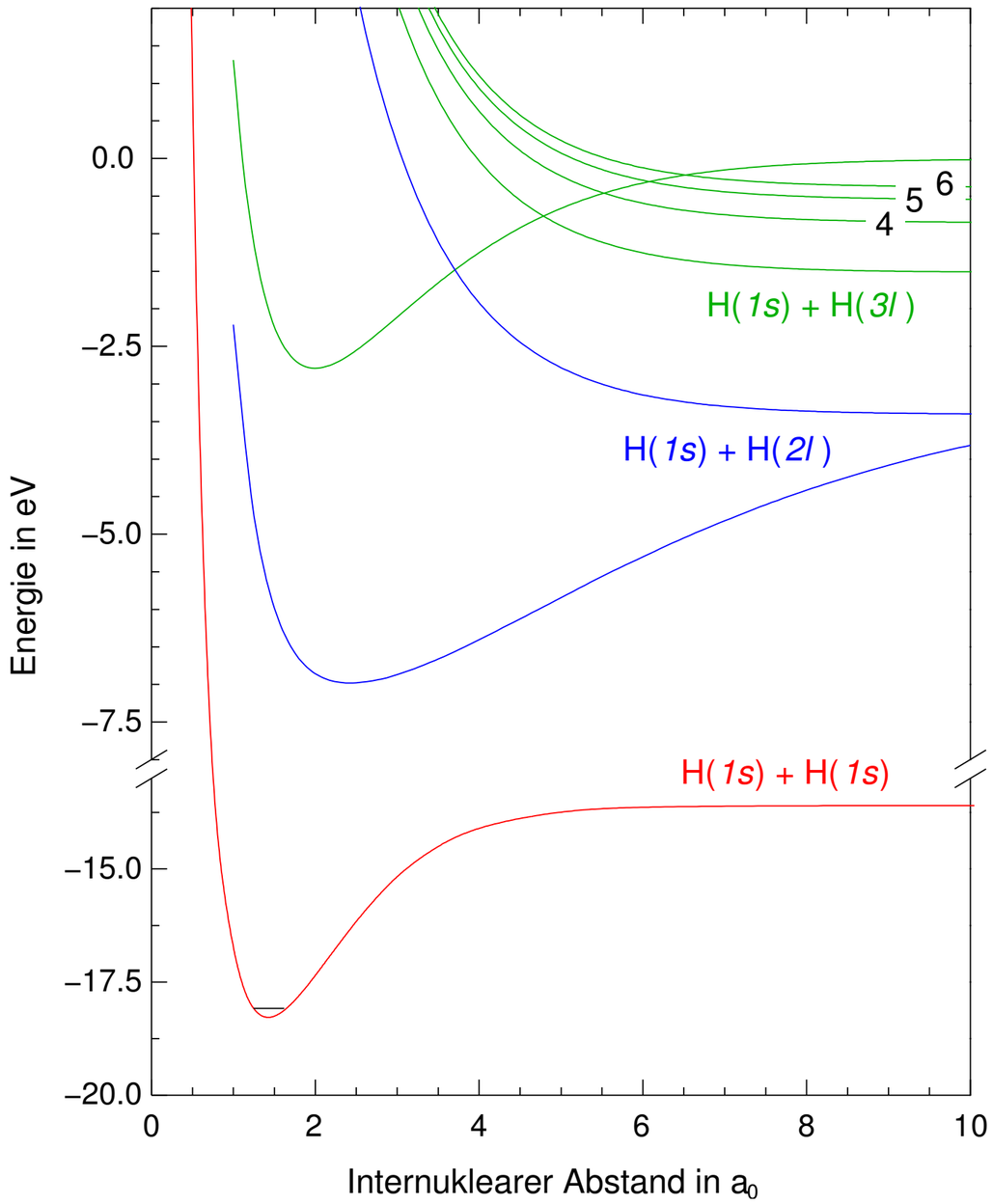
- Parity:

$$g \times g = g \tag{5}$$
$$u \times u = g \tag{6}$$
$$g \times u = u \tag{7}$$

- Spin:
  $\psi^{(a)} \equiv \psi^{(b)}$: *singlet*
  $\psi^{(a)} \neq \psi^{(b)}$: *singlet* or *triplet*

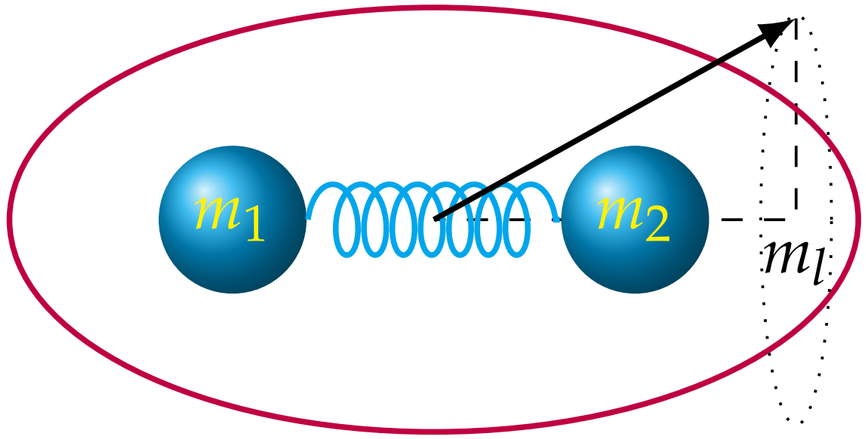
Term symbol: ${}^{2S+1}\Lambda^{(+,-)}_{(g,u)}$

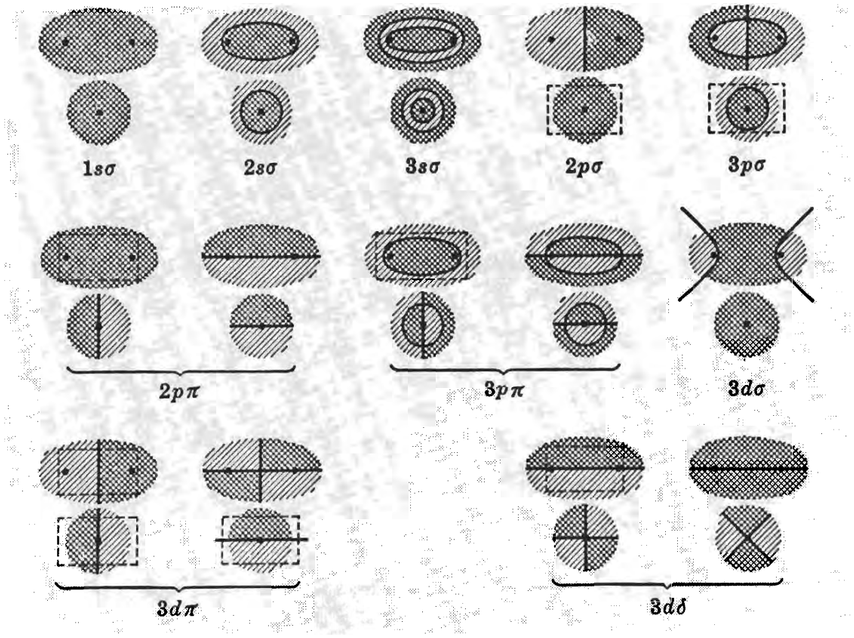
Potential energy surfaces; H_2

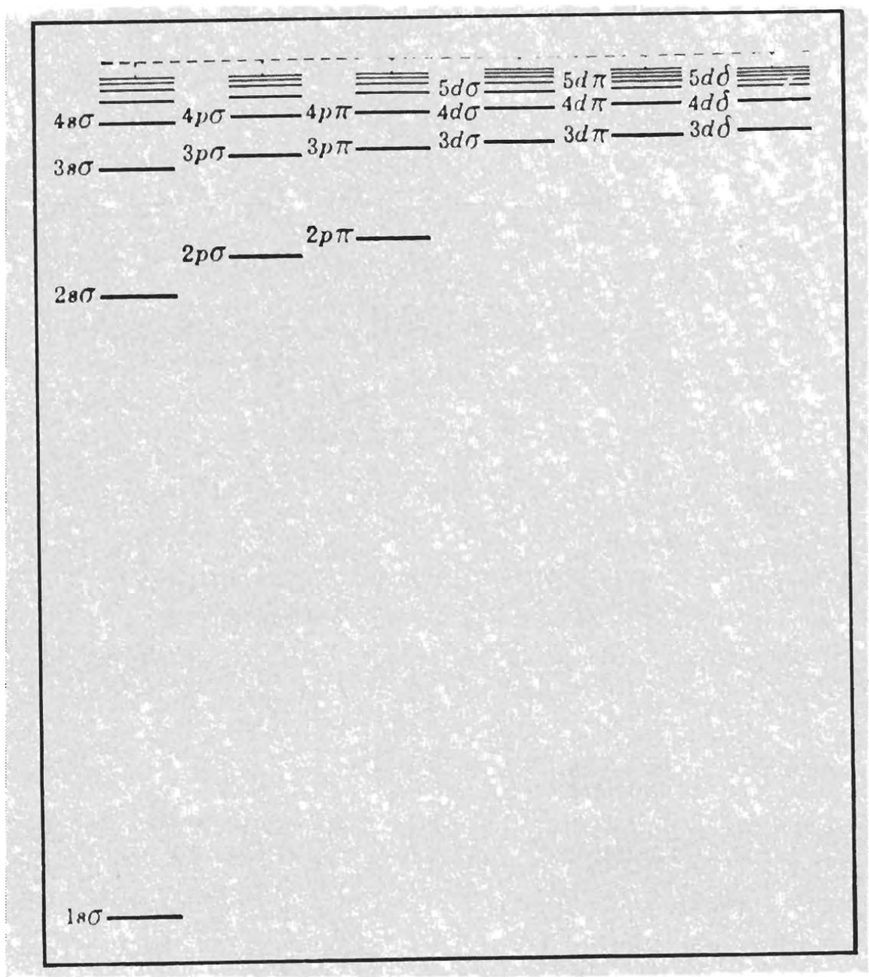


$$H_\mathrm{e}\left(\vec{r},\vec{R}\right)\Psi_\mathrm{e}\left(\vec{r};\vec{R}\right) = V\left(\vec{R}\right)\Psi_\mathrm{e}\left(\vec{r};\vec{R}\right)$$

United Atom picture





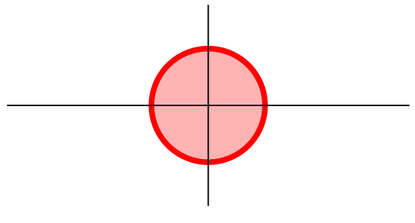


for $r \longrightarrow 0$: $H_2^+ \longrightarrow He^+ - n, l$ "as in atom"

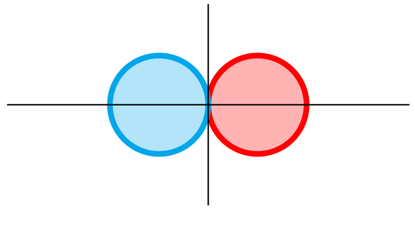
- m_l can have values $-l \ldots l$
- Only $|m_l| = \lambda$ is preserved and a good quantum number ($\lambda = 0, 1, 2 \Rightarrow \sigma, \pi, \delta$)
- σ-orbitals: symmetric about internuclear axis.
- π-orbitals: 1 nodal plane containing internuclear axis, always doubly degenerate.

Electronic angular momentum
Orbital symmetry

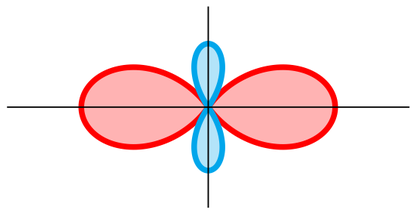
σ orbital possesses rotational symmetry around the internuclear axis



π orbital has one nodal plane containing the internuclear axis



δ orbital has two nodal planes containing the internuclear axis



Principal quantum number n associated with a function that has $n-1$ nodes.
For a σ orbital these are all radial.

Azimuthal quantum number l specifies the number of angular nodes ($l = 0, \ldots n-1$).

Therefore

l angular nodes

$n-l-1$ radial nodes

Multi-electron molecule

- Every electron approximately sees an effective field of the other electrons and nuclei (mean field; Hartree-Fock).
- The wavefunction can be written as

$$\psi = \prod_i^N \chi_i(q_i) \tag{25}$$

- $\chi_i(q_i)$ are one-electron wavefunctions (molecular orbitals) that can be written as linear combination of atomic orbitals (LCAO)
- ψ must change sign (antisymmetric) if any electrons i and j are exchanged ($\rightarrow$ Slater determinant)
- Obtained electronic states are characterized by *total orbital angular momentum*

$$\Lambda = \left| \sum_i m_{l_i} \right| = \left| \sum \pm \lambda_i \right| \tag{26}$$

  States are then denoted $\Sigma, \Pi, \Delta \ldots$
- The overall spin

$$S = \sum_i s_i \tag{27}$$

  determines the *multiplicity* $2S + 1$.
- general term symbol:

$$^{2S+1}\Lambda \tag{28}$$

Homonuclear Molecules
gerade/ungerade symmetry

When the two nuclei in the molecule are identical (i. e., have the same mass and charge), the orbital angular momentum function can only be

- symmetric (even, *gerade*), or
- anti-symmetric (odd, *ungerade*)

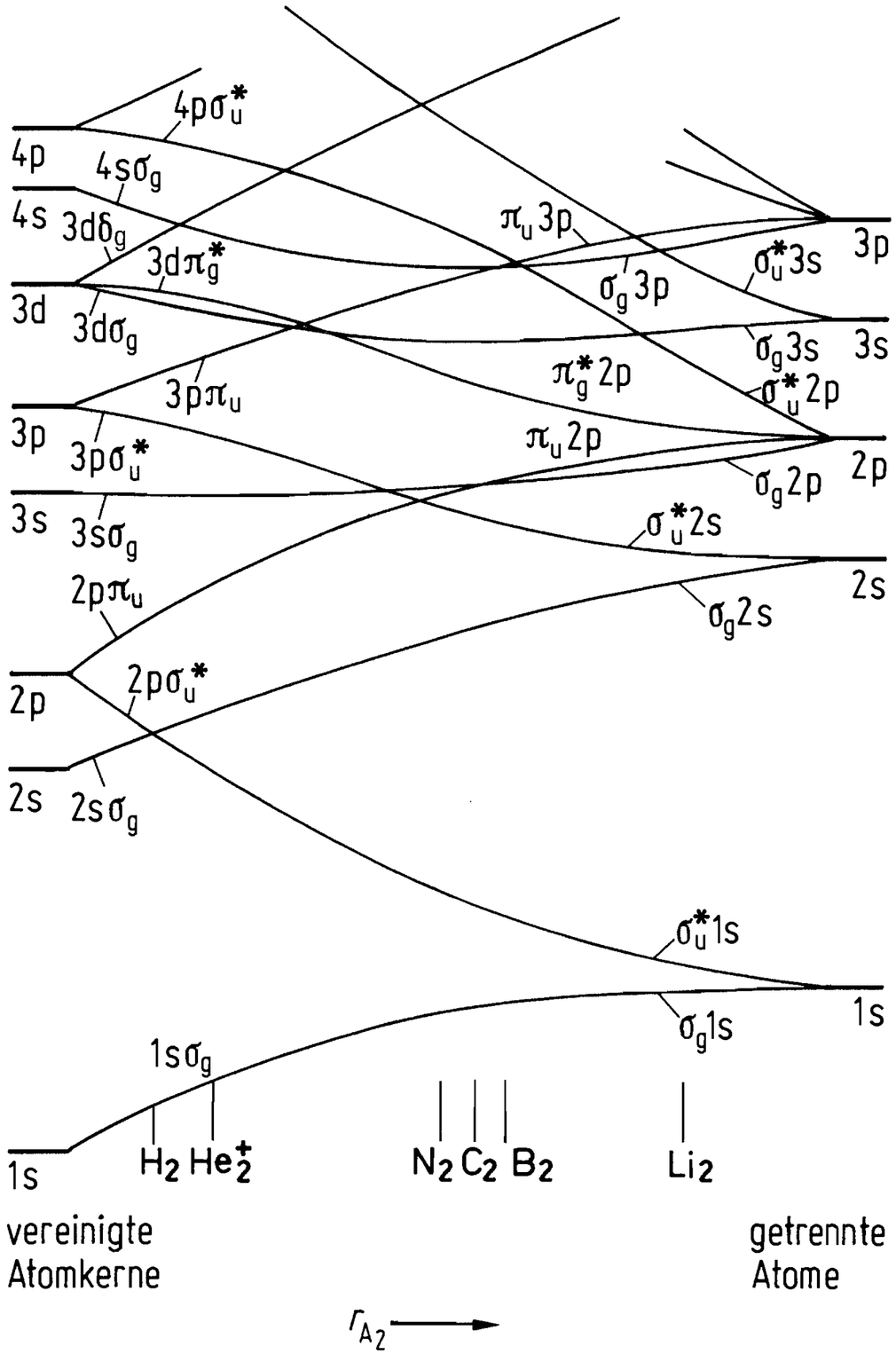
with respect to the inversion symmetry (point reflection at center of symmetry) in the molecule.

- one-electron wavefunctions:
  - g (gerade) for even l in united atom
  - u (ungerade) for odd l in united atom

  Molecular orbitals are described as $\sigma_g, \sigma_u, \pi_g, \pi_u, \ldots$
- many-electron systems:
  - g (gerade) for even number of odd orbitals
  - u (ungerade) for odd number of odd orbitals

Homonuclear Molecules

Correlation diagram between united atoms and separated atoms picture



Spin alignment

- All states with $\Lambda \geq 1$ ($\Pi, \Delta, \ldots$) are double degenerate (namely "$\pm\Lambda$").
- Different ways to create $\Lambda = 0$ lead to distinctly different Σ-states!
  For a configuration of two π orbitals one obtains

  $\Lambda = 2$: $\leftarrow\leftarrow$ or $\rightarrow\rightarrow$

  Exactly degenerate for non-rotating molecule

  $\Lambda = 0$: $\rightarrow\leftarrow$ or $\leftarrow\rightarrow$

  - Only degenerate to first approximation
  - In higher order approximations the sum- and difference-wavefunctions are not really degenerate
  - Symmetry with respect to reflection at any plane through the internuclear axis

    Σ^+ Symmetric with respect to reflection at any plane through the internuclear axis.

    Σ^- antisymmetric with respect to reflection at any plane through the internuclear axis.

- For the $\pi\pi$ configuration (e.g. in the BH molecule which is the united C atom, $(1s)^2(2s)^2(2p)^2$ in the molecular $(1s\sigma)^2(2s\sigma)^2(2p\pi)^2$ configuration), we then get the following states:

$$^1\Sigma^+, \, ^1\Sigma^-, \, ^1\Delta, \, ^3\Sigma^+, \, ^3\Sigma^-, \, ^3\Delta \tag{29}$$

Term symbol
Electronic state label

$$^{2S+1}\Lambda^{(+,-)}_{(u,g)}$$

- Λ: $\Sigma, \Pi, \Delta, \Phi, \ldots$
- $(+,-)$: doubly degenerate ($\pm\Lambda$)

different ways to create $\Lambda = 0$, leading to distinctly different Σ-states:

$\Sigma^{\pm}$: symmetric (+) or antisymmetric (-) with respect to reflection at any plane through the internuclear axis

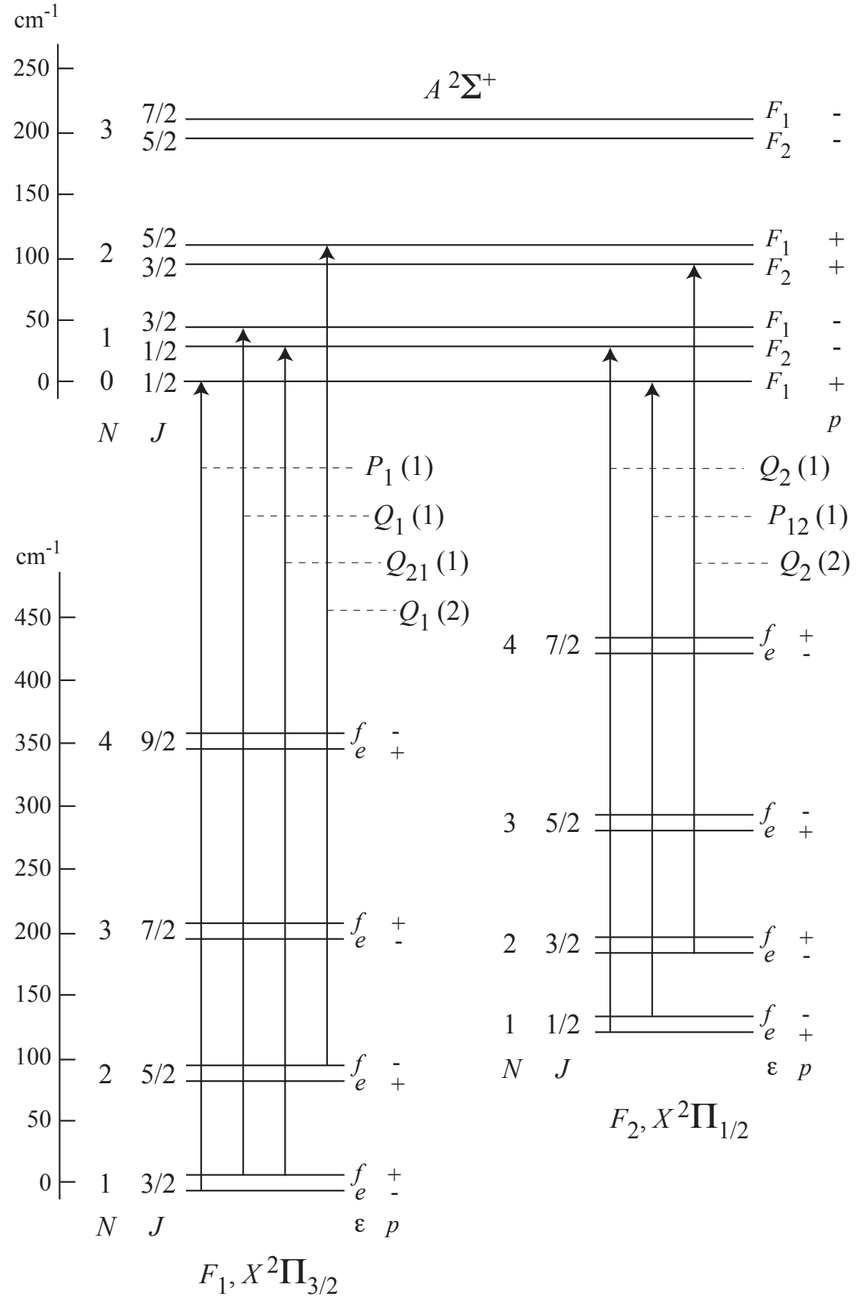
Multi electron molecules

Electronic configurations of OH

- Symmetrization postulate of QM (Pauli-principle) forbids putting all nine electrons of into lowest orbital. Therefore the configuration of the lowest electronic state of OH is $^2\Pi$:

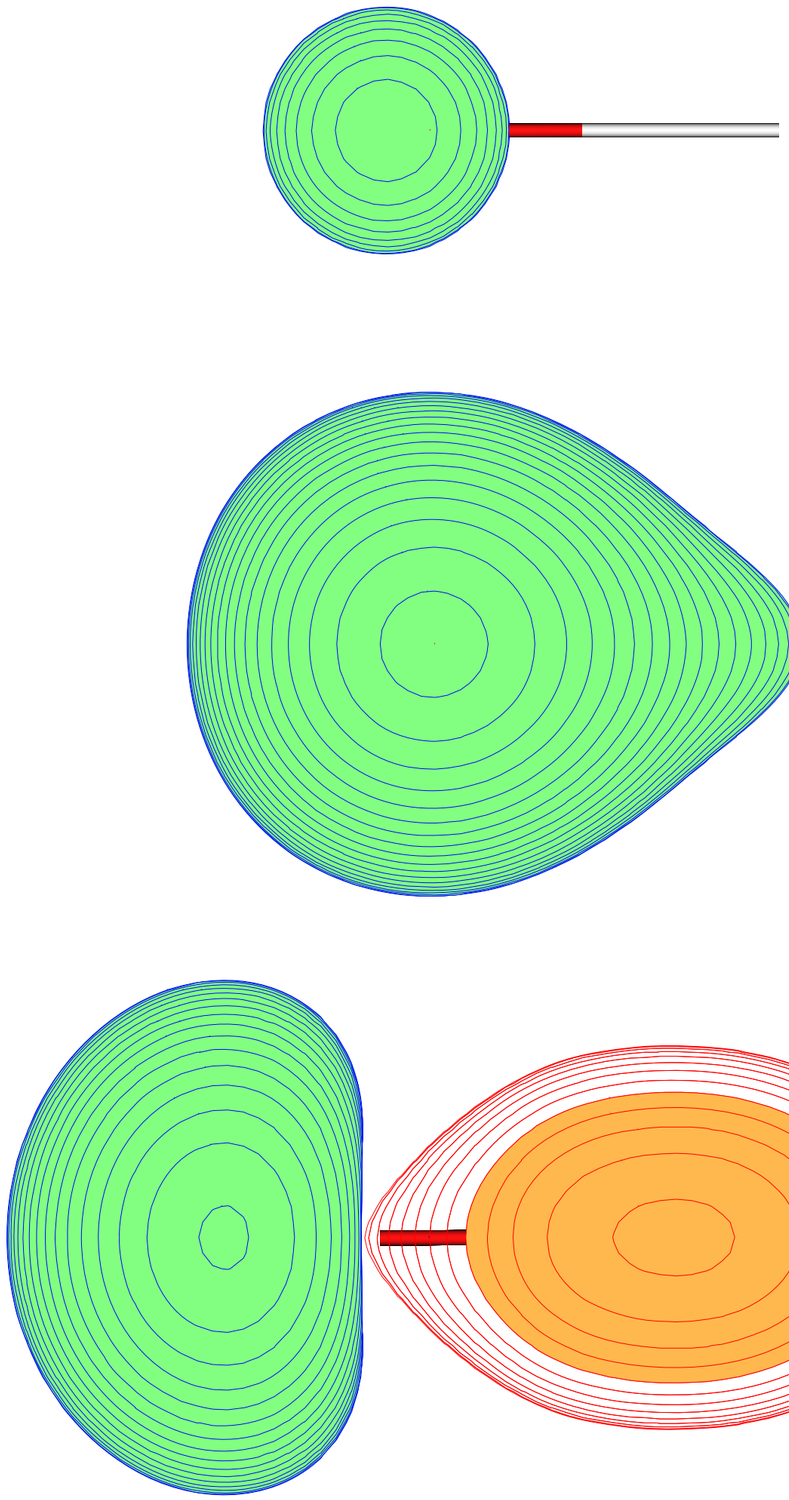
$$(1s\sigma)^2(2s\sigma)^2(2p\sigma)^2(2p\pi)^3$$

- The first electronically excited state corresponds to a $(1s\sigma) \rightarrow (2p\pi)$ ($\Delta n = 1$) excitation, resulting in a $^2\Sigma^+$ state.
- The excitation is in the UV (308 nm, 32500 cm^{-1}), showing the energy scale of the electronic states.



Molecular orbitals of OH

United atoms orbital $1s\sigma$



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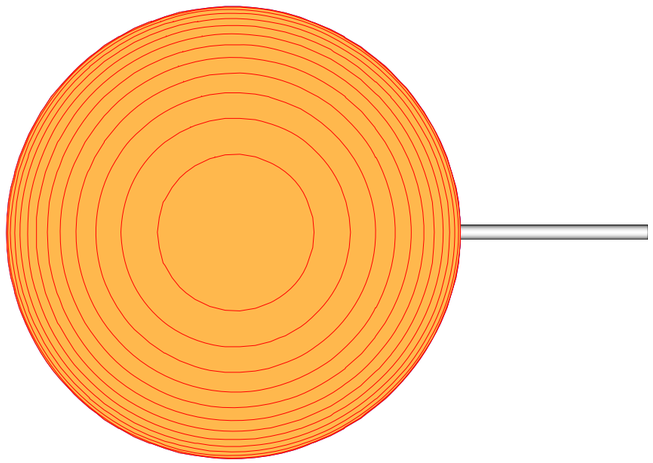


Gaussian 2003 C.02, MP2/aug-cc-pVTZ

Parity

Rotational (eigen-) states are characterized by *overall symmetry properties*; most importantly: **parity**

- \+ Overall eigenfunction remains unchanged for an inversion of all particles (electrons and nuclei at coordinates $\vec{r}$) through the origin
- \- Overall eigenfunction changes sign for an inversion of all particles (electrons and nuclei at coordinates $\vec{r}$) through the origin

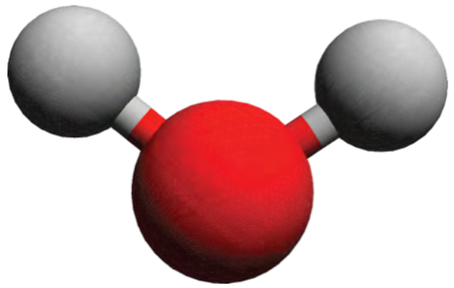
$$total : P\Psi(\vec{r}) = \pm\Psi(-\vec{r}) \tag{30}$$

$$electronic : P\Psi_e(\vec{r}) = (-1)^{i+j}\Psi_e(-\vec{r}) \text{ with } i = \begin{cases} 0 \hat{=} g \\ 1 \hat{=} u \end{cases} \text{ and } j = \begin{cases} 0 \hat{=} + \\ 1 \hat{=} - \end{cases} \tag{31}$$

$$vibrational : P\Psi_v(\vec{r}) = \Psi_v(-\vec{r}) \tag{32}$$

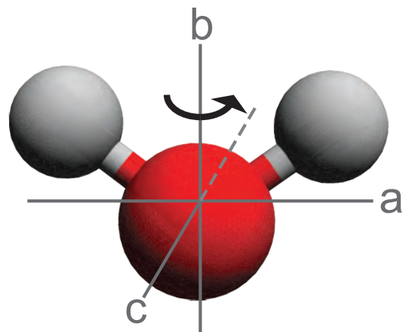
$$rotational : P\Psi_r(\vec{r}) = (-1)^J\Psi_r(-\vec{r}) \tag{33}$$

Furhter details: nuclear-spin hyperfine structure
Nuclear-spin isomers of water (H_2O)

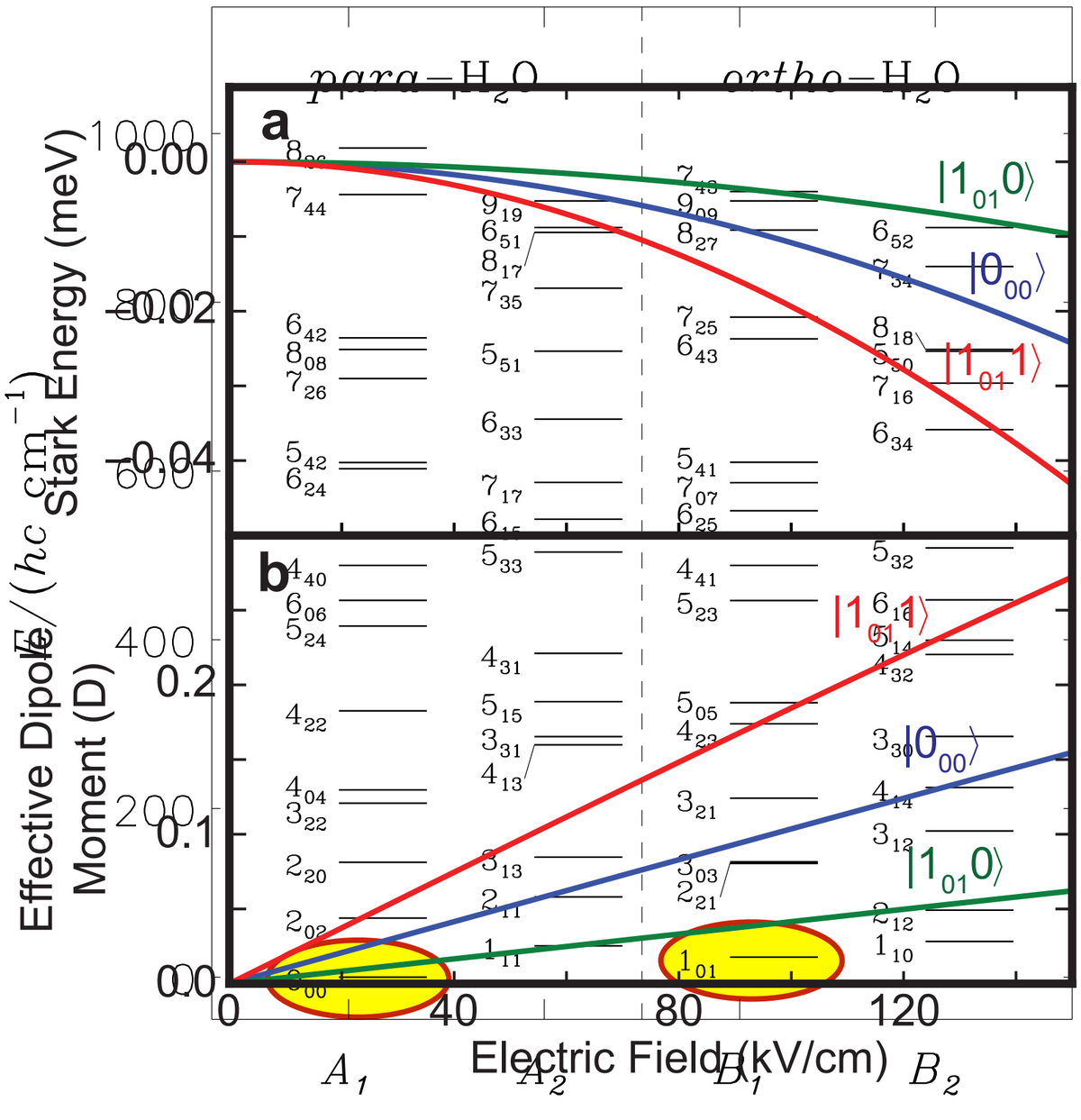


$$(12)\Psi = -\Psi$$

$$\Gamma_{\Psi_{\rm tot}} = \Gamma_{\Psi_{\rm ns}} \otimes \Gamma_{\Psi_{\rm rve}}$$



	Ψ_{spin}	Ψ_{rve}
ortho	$\downarrow\downarrow, \uparrow\uparrow, (\uparrow\downarrow + \uparrow\downarrow)$	
	I = 1 **S**	K_a+K_c = odd **A**
para	$(\uparrow\downarrow - \uparrow\downarrow)$	
	I = 0 **A**	K_a+K_c = even **S**



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We are looking for motivated colleagues, please see https://www.controlled-molecule-imaging.org/careers or contact me directly.