

MOLECULESfew K - few 10³ K

Observed in cooler, denser regions

Such as?

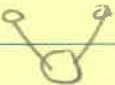
- Cool star atmospheres
- Planetary atmospheres
- Interstellar molecular clouds

The most tightly bound molecules

are diatomic e.g. CO, OH, H₂

In even denser, cooler regions

see polyatomic

e.g. H₂O 

Degrees of freedom

1. Electronic
2. Vibrational
3. Rotational

Energy splittings

UV

IR

Radio

We'll see

$$E_{elec} : E_{vib} : E_{rot} \sim 1 : \left(\frac{m_e}{m_{nuc}}\right)^{\frac{1}{2}} : \left(\frac{m_e}{m_{nuc}}\right)$$

The most abundant molecule is?

H₂But H₂, which is homonuclear,has no dipole moment in ground state,
so its rotational transitions are forbidden.H₂ rot transitions are quadrupole.H₂ does have allowed elec (UV) & vib (IR) trans.

CO is most commonly observed molecule.

Hertzberg, G (1950) Spectra of Diatomic Molecules

11.2

Diatomic molecules: electronic level notation

To calculate electronic levels of molecules,
good approximation to say $V_{elec} \gg V_{nuc}$ (why?)
So electronic wavefunction "instantly" adjusts to positions of nuclei.
Born-Oppenheimer approximation.

(i) Electronic angular momentum Λ about molecular axis.

Whereas

(a) in atom, elec field of the single nucleus is spherically symmetric, so orbital elec ang mom is conserved so L is good quantum number,

(b) in diatomic molecule, elec field of nuclei is symmetric only about molecular axis,



so only projection of orbital elec ang mom about axis is conserved

Abs value of projection denoted

$$\Lambda = \Sigma \quad \Pi \quad \Delta \quad \Phi \quad \Gamma$$

0 1 2 3 4

analogous to S P D F G

Q: Ignoring vib & rot degrees of freedom, and spin degrees of freedom,

how many electronic Λ states are there?

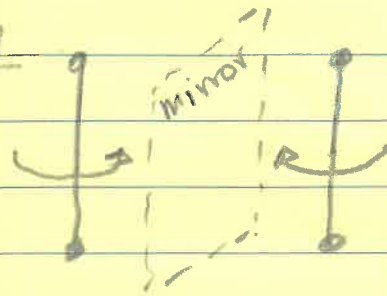
A. 1, if $\Lambda = 0$, 2 if $\Lambda \neq 0$.

Λ^\pm even/odd electron parity.

11.3

(ii) Reflection & Λ -doubling

If $\Lambda \neq 0$,
then there are
2 directions of
motion of electrons
about molecular axis.



If nuclei are not rotating, then
the two Λ states are degenerate.
If nuclei are rotating, then
the two Λ states are split
(slightly, because rotation is slow)
= " Λ -doubling".

(iii) Reflection is special case of Σ

If $\Lambda = 0$, i.e. term is Σ ,
then reflection of molecule through
axis transforms electronic wavefunction

$$\psi_\Sigma \longrightarrow \begin{matrix} \pm \\ \uparrow \\ \psi_\Sigma \end{matrix} \begin{matrix} \text{even} \\ \text{odd} \end{matrix}$$

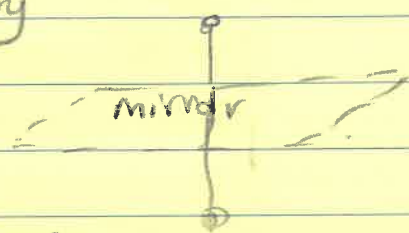
2 reflections
= unity

Write Σ^+ even under reflection
 Σ^- odd

Only one of Σ^+ or Σ^- occurs.

\pm = electron parity!

Same charge, more generally
(iv) Homonuclear molecules (H_2, O_2, \dots)
have an additional symmetry
under reflections through
midplane of molecular axis.



Reflection of electronic wavefunction ψ_{elect}
(leaving nuclei in place) transforms

$$\psi \rightarrow \begin{matrix} \pm \\ \uparrow \\ \psi \end{matrix} \quad \begin{matrix} \text{gerade (German "straight")} \\ \text{ungerade} \end{matrix}$$

2 reflections
= unity

Denoted

$$\Lambda_g^+$$

gerade
+

$$\Lambda_u^-$$

ungerade
-

(v) Electronic spin

is conserved in absence of spin-orbit
or spin-spin interaction.

Notation for molecular term with
total electronic spin S same as for atoms

$$2S+1 \Lambda_g^u$$

(vi) Empirical designations

In atoms, electronic configuration ($1s^2 2s^2 \dots$), along with term ^{2S+1}L , serve to specify electronic state (ignoring fine structure & hyperfine structure).


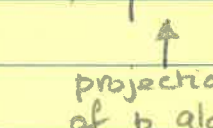
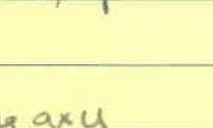
In molecules, the labeling of the electronic configuration is more ad hoc, not uniform in logic (blame history).

X denotes ground state

A, B, C, ... denotes levels with same spin S (usually 0 or $\frac{1}{2}$) as ground state

a, b, c, ... denotes levels with spin S different from ground state

Ex/ H_2

spin singlet	ground state X $^1\Sigma_g^+$	[A]	B $^1\Sigma_u^+$	C $^1\Pi_u$	E, F $^1\Sigma_g^+$
equiv to	1s, 1s	[1s, 2s σ]	1s, 2p σ	1s, 2p π	1s, 2s σ + 2p σ
		missing			
			↑ projection of p along axis		

spin triplet	a $^3\Sigma_g^+$	b $^3\Sigma_u^+$	c $^3\Pi_u$
	1s, 2s σ	1s, 2p σ	1s, 2p π

Q: How identify (theoretically) elec config?

A: Slowly pull molecule apart



11.5'

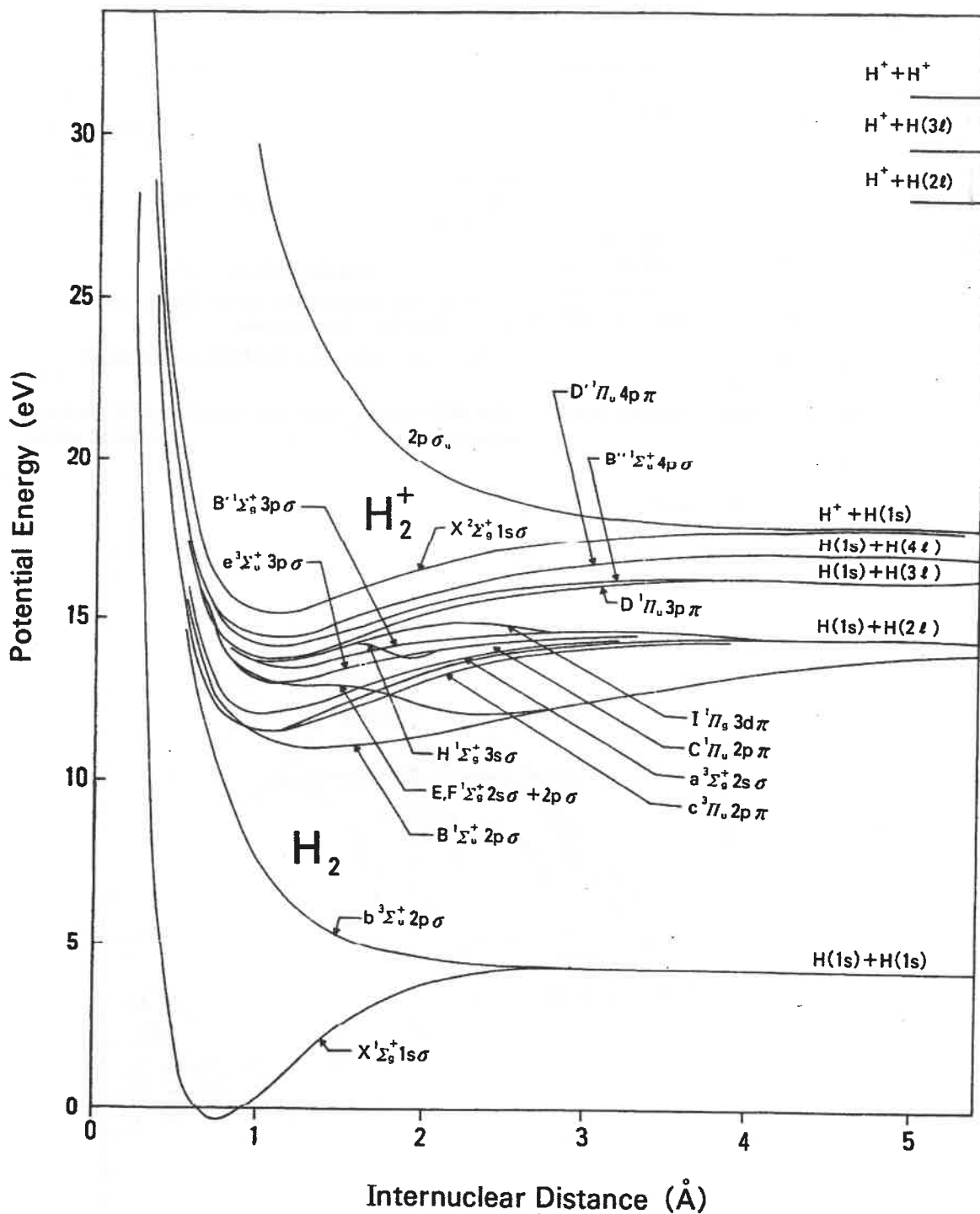
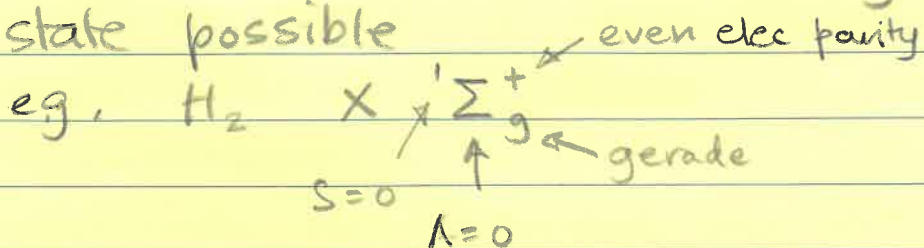


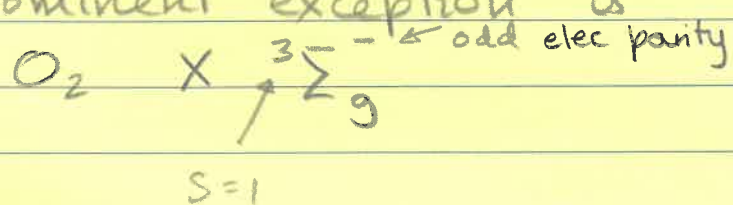
FIG. 1. Some important energy levels of molecular hydrogen and molecular ion (see Ref. 5).

Ground electronic state

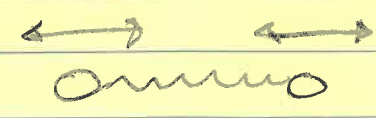
Empirically, the ground elec state of most molecules is the most symmetric state possible



A prominent exception is



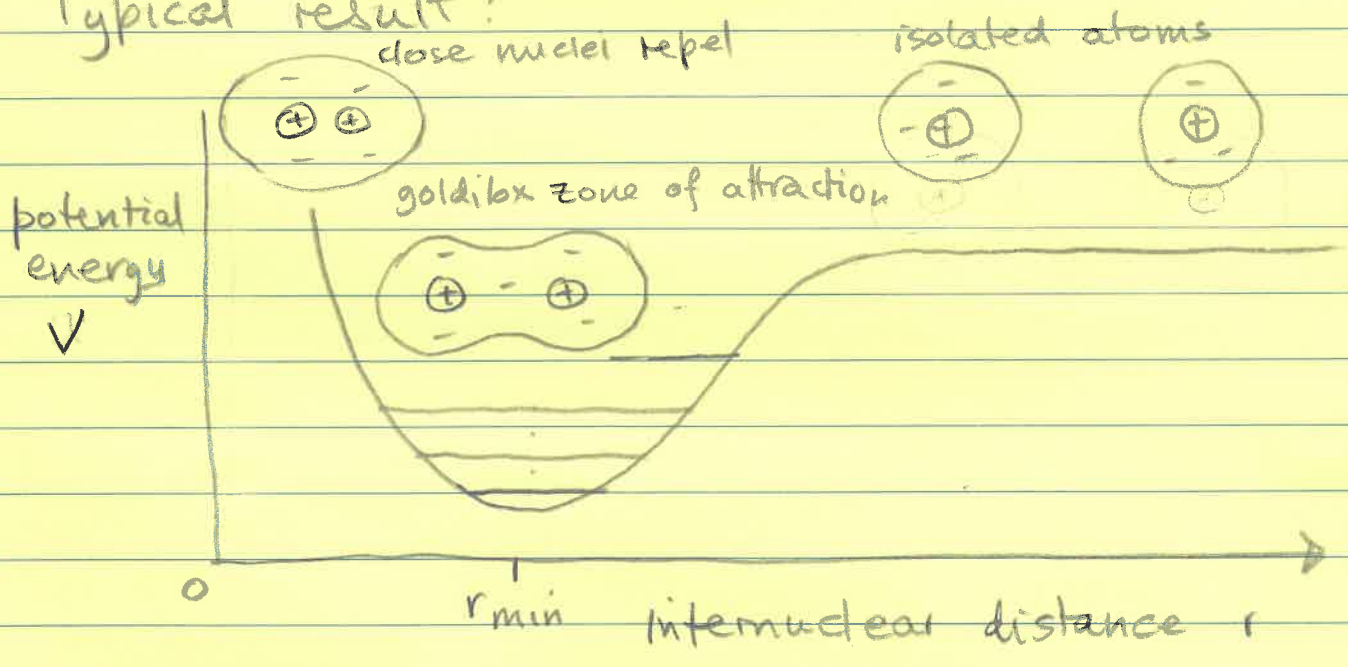
Diatomic molecules: vibrational energy levels



Each elec level is split into several vibrational energy levels.

Again, approximate electrons as adjusting "instantly" to position of molecules (Born-Opp), solve for elec. wavefunctions, hence energy, as function of fixed internuclear distance.

Typical result:



In vicinity of minimum, "force constant"

$$V \approx \frac{1}{2} k (r - r_{min})^2 + \text{const.}$$

Nuclear Hamiltonian is

$$H_{nuc} = \frac{p^2}{2m} + \frac{1}{2} k (r - r_{min})^2$$

\uparrow reduced mass of 2 nuclei \uparrow $= m \omega_{vib}^2$

This is Ham of quantum simple harmonic oscillator. Solutions have energy levels

$$E_{\nu} = \hbar \omega_{\text{vib}} \left(\nu + \frac{1}{2} \right) \quad \nu = 0, 1, \dots$$

\uparrow
 vib level number

$= \sqrt{\frac{k}{m}}$

The force constant k depends on the behavior of electrons in electric field of nuclei, so is independent of mass of nuclei. Thus

$$E_{\text{vib}} \equiv \hbar \omega_{\text{vib}} \propto \sqrt{\frac{m_e}{m_r}} \text{ atomic units}$$

\leftarrow
 reduced mass of 2 nuclei.

Ex / Potential energy curves of H_2 HD D_2 $\oplus - \oplus$

are all the same, But E_{vib} differ, $\propto \frac{1}{\sqrt{m}}$

Departure from STO approximation

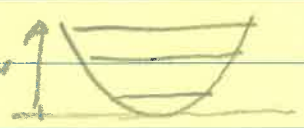
Potential energy curves are not precisely quadratic

Common to expand E_{ν} as

$$E_{\nu} = E_{\text{vib}} \left(\nu + \frac{1}{2} \right) + E_{\text{vib}}^{(1)} \left(\nu + \frac{1}{2} \right)^2 + \dots$$

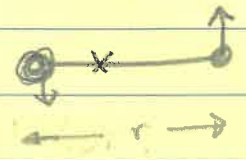
different for different electronic levels

= 0 by construction at $\nu = -\frac{1}{2}$



Diatomic molecules; rotational energy levels

Born-Oppenheimer approx
rotational constant as rigid



Diatomic molecular Hamiltonian (2 body problem)

μ relative momentum of nuclei

$$H = \frac{p_{nuc}^2}{2m} + V(r)$$

↑
reduced mass nuc separation

$$= \frac{p_r^2}{2m} + V(r) + \frac{\hat{J}^2}{2mr^2}$$

= H_{vib} = H_{rot}

Approximate $r = \text{constant}$ in H_{rot}
"rigid rotator" (part of Born-Opp approx).
Why?

Eigenvalue of \hat{J}^2 are ?

$$E_J = \frac{J(J+1)\hbar^2}{2mr^2}$$

$$= \frac{\hbar^2 J(J+1)}{2I}$$

where $I = mr^2 = \text{moment of inertia}$.

$$= B_v J(J+1)$$

↑
"rotational constant" (different for diff vib levels)

$r \approx a_0 = 1 \text{ atomic unit}$

so $E_J \sim \frac{m_e}{m} \text{ atomic units}$.

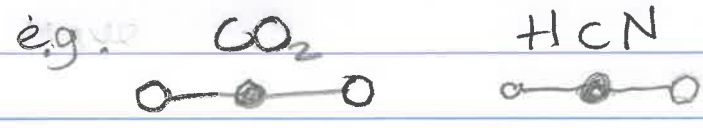
Polyatomic molecules: degrees of freedom
 If molecule contains N nuclei
 then there are

$$3N - 3$$

total dof translational dof
 do not affect internal structure

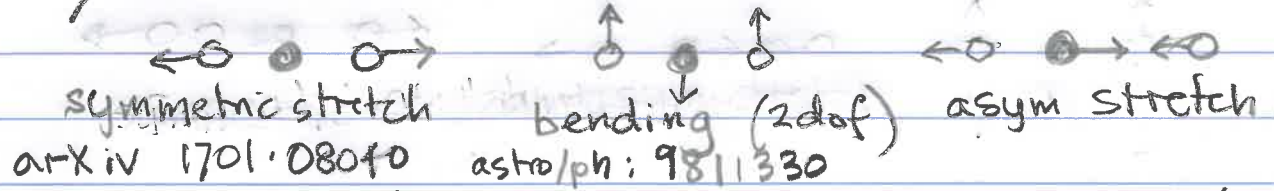
internal degrees of freedom,

Collinear molecules



have 2 rotational dof (no rot about axis),
 hence $3N - 5$ vibrational dof.

Ex/ CO2 $N=3 \Rightarrow 3N - 5 = 4$ vib dof



arXiv 1701.08040

astro/ph: 9811330

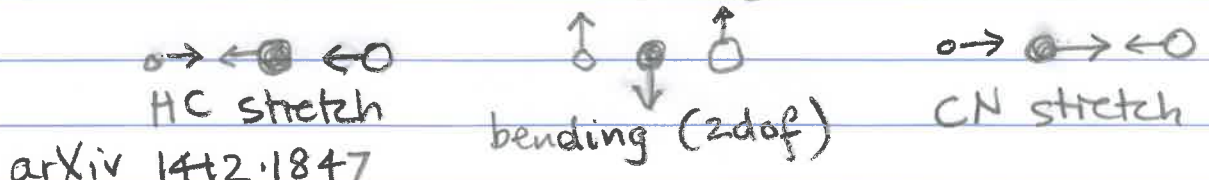
E_{vib}	1340 cm^{-1}	667 cm^{-1}	2349 cm^{-1}
\uparrow	$(7.46 \mu\text{m})$	$(15.0 \mu\text{m})$	$(4.26 \mu\text{m})$

$h\nu_v \approx E_{vib} (v + \frac{1}{2})$ ← rot about axis

Vib state notation $v_1 v_2 v_3$

$1 \text{ cm}^{-1} = 1.438777 \text{ K}$

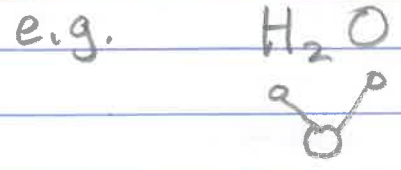
HCN $N=3 \Rightarrow N_{vib} = 4$



arXiv 1412.1847

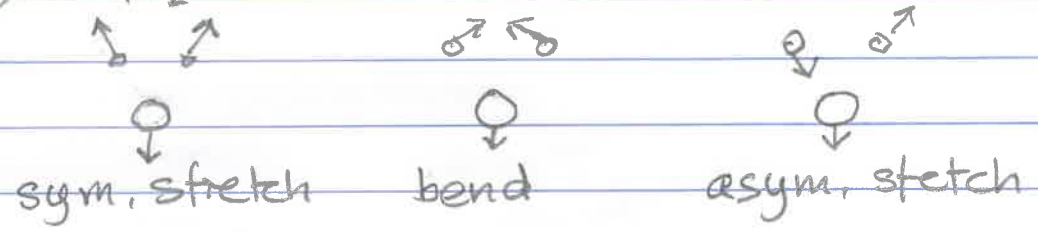
3314 cm^{-1}	715 cm^{-1}	2097 cm^{-1}
$(3.02 \mu\text{m})$	$(14.0 \mu\text{m})$	$(4.77 \mu\text{m})$

Non-collinear molecules: vibrational



have 3 rotational dof,
hence $3N-6$ vibrational dof.

Ex/ H2O $N=3 \Rightarrow 3N-6 = 3$ vib dof

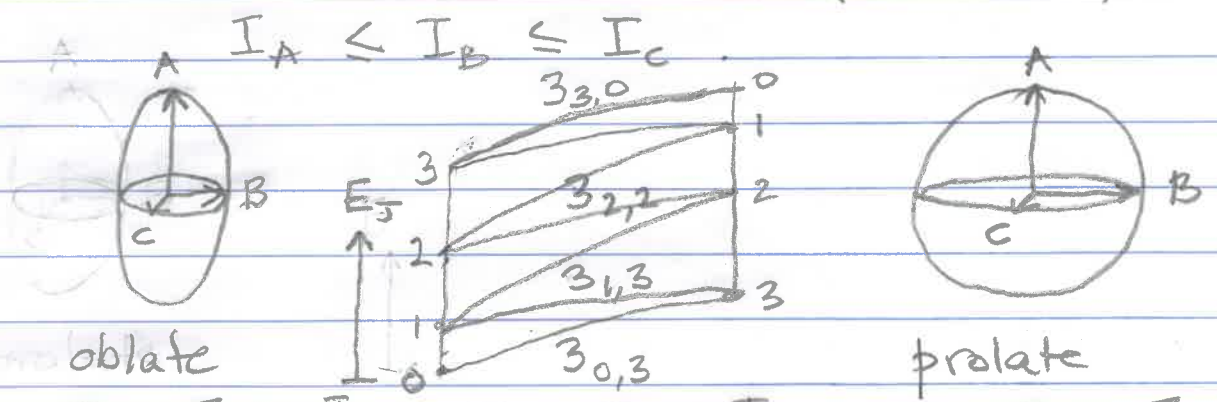


$E_{vib}: 3657 \text{ cm}^{-1}$ 1595 cm^{-1} 3756 cm^{-1}
 (2.73 μm) (6.27 μm) (2.66 μm)

Vib state notation: $\nu_1 \nu_2 \nu_3$

Non-collinear molecules: rotational

have 3 distinct moments of inertia,



$I_A < I_B = I_C$ $I_A < I_B < I_C$ $I_A = I_B < I_C$
 $E_J: BJ(J+1) + (A-B)K_A^2$ $BJ(J+1) + (C-B)K_C^2$

Rot state notation: J_{K_A, K_C}

$K_A, K_C =$ projection of \vec{J} along A, C axes.

Ex/ $J=3$, # states = $2J+1 = 7$, as above.

Newfield et al (1991)

1991ApJ...368...215N

11011

Rotational ENERGY LEVEL DIAGRAM FOR ORTHO-H₂O

Rotational ENERGY LEVEL DIAGRAM FOR PARA-H₂O

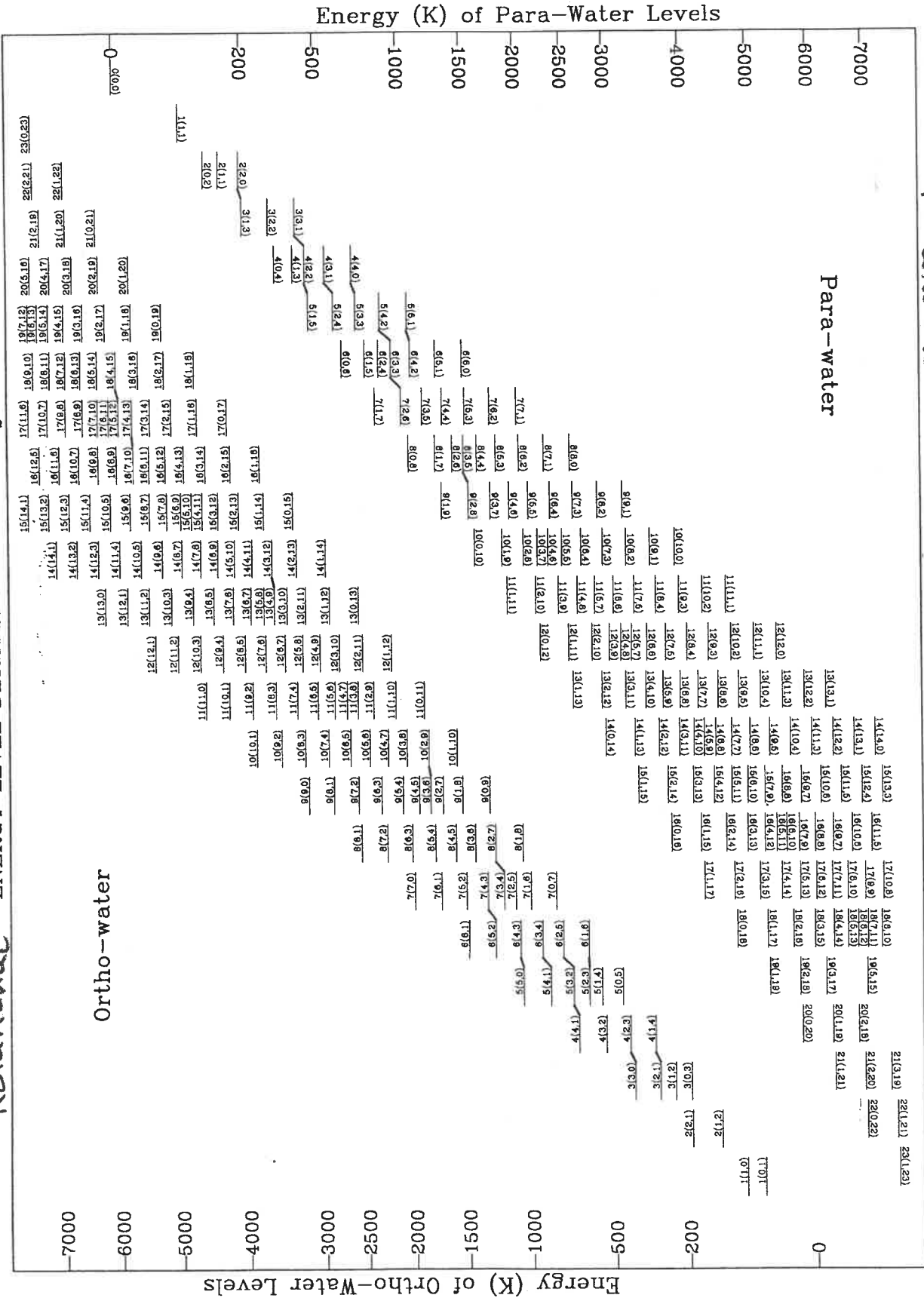


Fig. 1.—Energy level diagram for H₂¹⁶O. Each state is labeled with the quantum numbers J(K_a, K_c) and missing transitions are marked as solid lines connecting neighboring states.

Diatomic molecules: fine structure

Fine structure from interaction of electron spin \vec{S}_{elec} with \vec{L}_{elec} , \vec{S}_{elec} , \vec{L}_{nuc} .

Hund's cases (a) - (d) eg. $OH^2\pi_3$ maser

Hund case (a) (most common for $\Lambda \neq 0$)

Electron spin precesses around molecular axis much faster than molecule rotates.

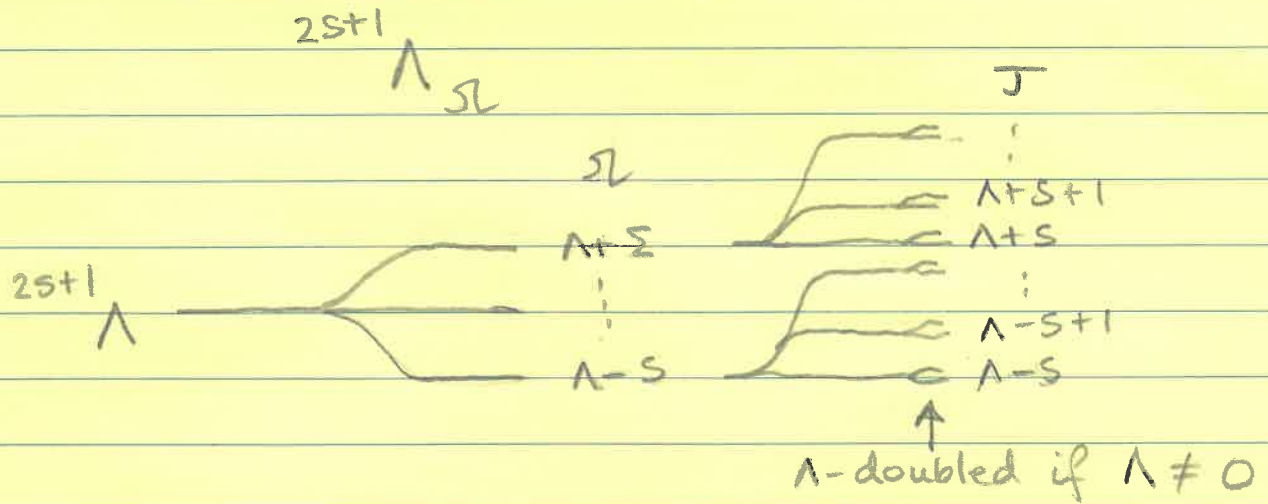


Projection of Σ of \vec{S}_{elec} along axis is good quantum number

$$\Omega \equiv \Lambda + \sum_{-S \text{ to } S} + \text{zero (why?)}$$

projection of \vec{L}_{elec} \vec{S}_{elec} \vec{L}_{nuc} along axis

Term notation



$$\vec{J} \equiv \vec{L}_{elec} + \vec{S}_{elec} + \vec{L}_{nuc} = \text{total ang mom (sans nuc spin)}$$

Total ang mom quantum number J takes values

$$J = |\Omega|, |\Omega+1|, \dots, \text{large}$$

Energy levels those of symmetric top

$$E = B J(J+1) + (A-B)\Omega^2$$

Hund case (b) (most common for $\Lambda = 0$)

Molecule rotates faster than elec spin precesses about axis.

Define

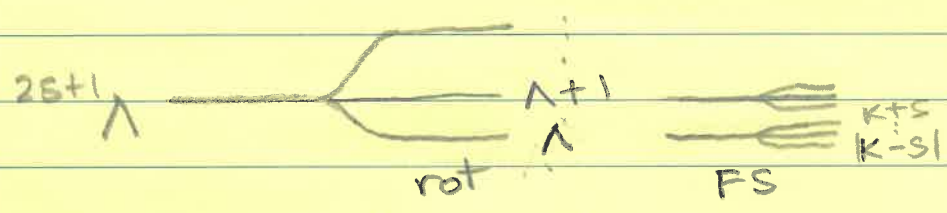
$$\vec{K} \equiv \vec{L}_{elec} + \vec{L}_{nuc} \quad \text{total orb ang mom}$$

Projection of \vec{K} along axis is

$$\Lambda = \Lambda + 0$$

Quantum number K takes values

$$K = \Lambda, \Lambda+1, \dots, \text{large } K$$



$$\vec{J} \equiv \vec{L}_{elec} + \vec{S}_{elec} + \vec{L}_{nuc}$$

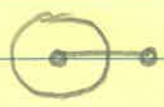
$$= \vec{K} + \vec{S}_{elec}$$

Quantum number J takes values

$$J = |K-S|, |K-S|+1, \dots, K+S$$

Hund case (c)

Eg. heavy molecules.
Electron cloud \sim atomic.



Hund case (d)

Highly excited electron moves slowly compared to molecular rot, sees molecule as \sim atom.



(Anti)symmetry of homonuclear molecule under nuclear exchange implies that nuclear orbital ang mom can be only even or only odd.

Total nuclear wavefunc must be :
even bosonic nuclei
odd fermionic nuclei

Symmetry is product of nuclear spin and orbital symmetries.

Nuclear spin symmetry is

$$\begin{matrix} + \\ - \end{matrix} (-)^{S_{nuc}} \begin{matrix} \uparrow \\ \uparrow \end{matrix}$$
 bosons
fermions
total nuclear spin

if max possible spin $\uparrow\uparrow$ always symm.

Symmetry of total elec + nuclear orb ang mom

$$\vec{K} = \vec{L}_{elec} + \vec{L}_{nuc}$$

is $(-)^K$.

Symmetry of elec orb ang mom is, for $\Lambda = 0$, \pm as Σ^\pm

so symm of nuc orb ang mom is

$$\begin{matrix} + \\ - \end{matrix} (-)^K \text{ at } \Sigma^\pm$$

(For $\Lambda \neq 0$, both electron symms Λ^\pm occur, so nuc orb symm can be even or odd.)

Net result total nuclear symmetry is

$$\begin{matrix} + \\ - \end{matrix} (-)^{S_{nuc}} \times \begin{matrix} + \\ - \end{matrix} (-)^K \stackrel{\text{must}}{=} \begin{matrix} + \\ - \end{matrix}$$

\uparrow boson
 \uparrow fermion

\uparrow Σ^+
 \uparrow Σ^-

ie. sign of $\begin{matrix} + \\ - \end{matrix} (-)^K \stackrel{\text{must}}{=} (-)^{S_{nuc}}$

\uparrow Σ^+
 \uparrow Σ^-

Examples

1. H_2 $^1\Sigma_g^+$ spin- $\frac{1}{2}$ nuclei
 ground

S_{nuc}	K	name
0 (singlet)	0, 2, 4, ...	para
1 (triplet)	1, 3, 5, ...	ortho

Probability of nuclear spin flip is so (hyperfine) small that para- and ortho-hydrogen behave almost like 2 independent species

2. O_2 $^3\Sigma_g^-$ spin-0 nuclei
 ground

S_{nuc}	K
0	1, 3, 5, ...

3. N_2 $^1\Sigma_g^+$ spin-1 nuclei
 ground

S_{nuc}	K	name
0, 2	0, 2, 4, ...	ortho (+)
1	1, 3, 5, ...	para

Ortho is species with greater statistical weight.