

MOLECULAR SPECTRA

Pure rotational spectra (no elec, vib transition)

Selection rules for em/abs of elec dipole rad

1. Molecule must have permanent dipole moment

$$\vec{d} = \vec{d}_{\text{nuc}} + \vec{d}_{\text{elec}}$$

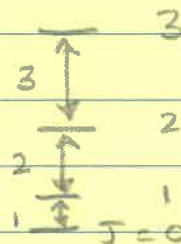
2. $\Delta J = -1$ em
 $+1$ abs

3. $\Delta J = 0$ also allowed

for asymmetric tops ($I_A < I_B < I_C$)

Note that $\vec{J} = \vec{K} + \vec{S}_{\text{elec}}$

So $\Delta K = \Delta J$ in pure rot transition.



Rotational spectra of homonuclear molecules

H_2, D_2, O_2, \dots in ground elec term $\Lambda = 0$ have no dipole moment.

But do radiate by quadrupole radiation

$$\Delta K = \Delta J = -2 \text{ em}$$

$$+2 \text{ abs}$$

Ro-vibrational spectra

= vibrational transition $v_u - v_L$

together with rotational transition.

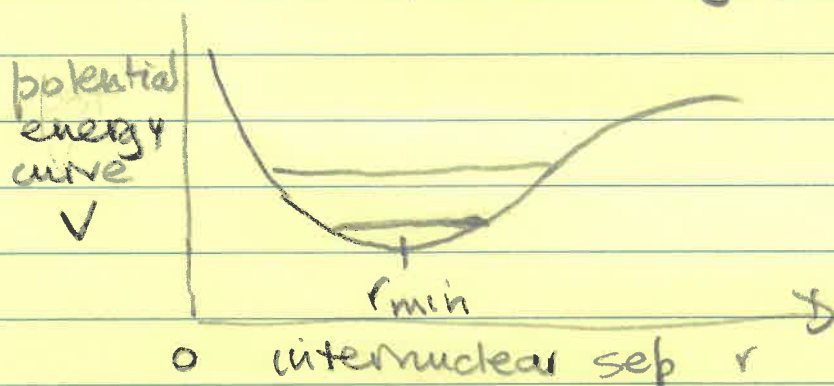
Polarizability eg. oscillating em photon field

Apply external elec field \vec{E} to molecule.

Induced dipole moment is Herzberg p. 82

$$\vec{d} = \alpha \vec{E}$$

α polarizability (a matrix)



Expand α as Taylor series about $r = r_{min}$:

$$\alpha = \alpha_0 + \alpha_1 (r - r_{min}) + \dots$$

Then

$$\langle \psi_u | \vec{d} | \psi_L \rangle = \vec{E} \left\{ \alpha_0 \langle \psi_u | \psi_L \rangle + \alpha_1 \langle \psi_u | r - r_{min} | \psi_L \rangle + \dots \right\} \vec{E}$$

\uparrow quantum wavefunctions \uparrow STO

Linear term $\neq 0$ only for $v_u = v_L + 1$.

So to extent that

(i) higher terms of polarizability small;

(ii) STO good approximation,

get vibrational selection rule

$$\Delta v = -1 \text{ em}$$

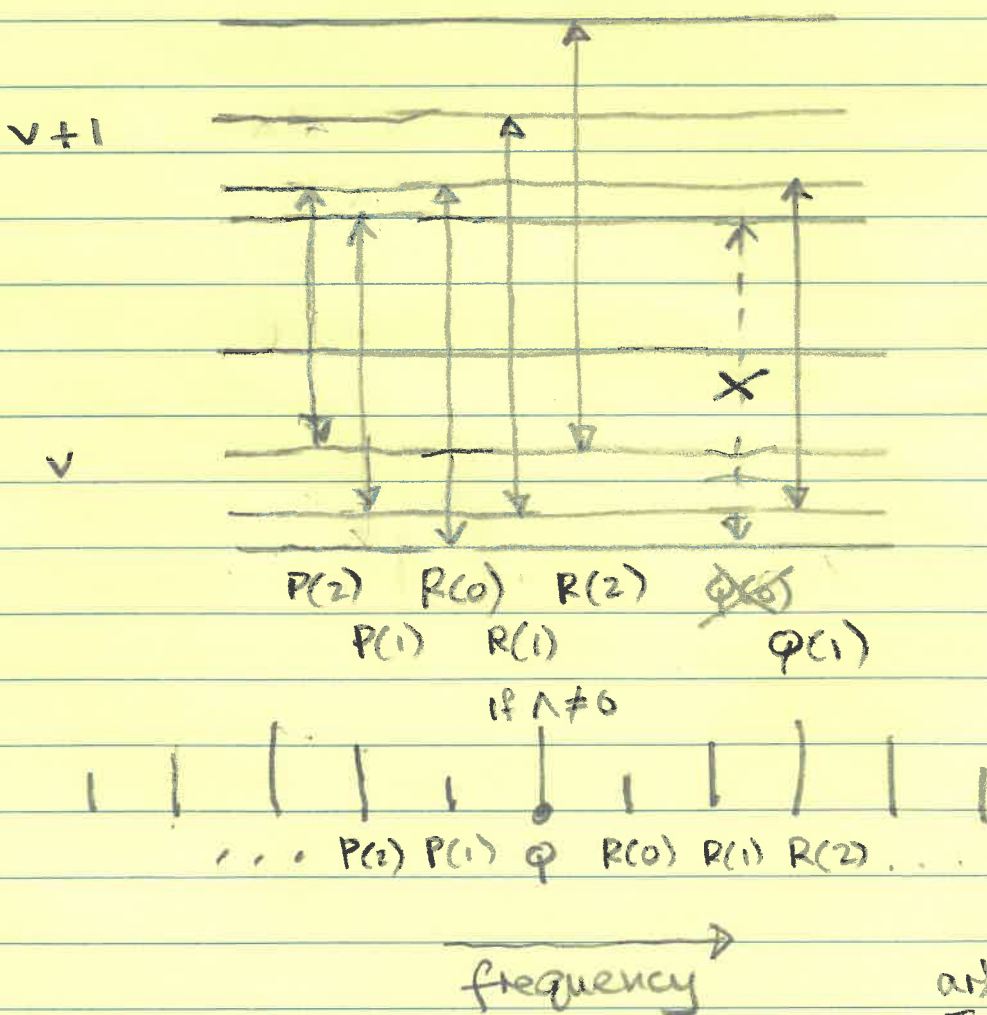
$$+1 \text{ abs}$$

Selection rules for em/abs of elec dipole rad for ro-vibrational spectra:

- 1. Linear polarizability $\alpha_1 \neq 0$ } vib rules
- 2. $\Delta v \approx \pm 1$ }
- 3. $\vec{d}_{perm} \neq 0$ }
- 4. $\Delta J = \pm 1$ ($\Lambda = 0$) } rot rules
- 5. $\Delta J = 0, \pm 1$ ($\Lambda \neq 0$) but $J=0 \neq 0$ }

Notation for transition:

$$(\nu_u - \nu_L) \begin{cases} P(J_L) & J_u = J_L - 1 \\ Q(J_L) & J_u = J_L \\ R(J_L) & J_u = J_L + 1 \end{cases} \quad (\Lambda \neq 0)$$



Transitions with $\Delta J = \pm 2$

occur in:

- homonuclear molecules eg, H_2 , N_2 , O_2 which have no permanent elec dipole moment
- "Raman" scattering
= scattering of photons of any frequency



Nomenclature

$$(\nu_u - \nu_L) \left\{ \begin{array}{l} O(J_L) \quad J_u = J_L - 2 \\ P(J_L) \quad J_u = J_L - 1 \\ Q(J_L) \quad J_u = J_L \quad J_L \neq 0 \\ R(J_L) \quad J_u = J_L + 1 \\ S(J_L) \quad J_u = J_L + 2 \end{array} \right.$$

1509.06607 1507.06650 Fig 1

12.5

Example ro-vibrational lines

arXiv: 1304.4961

^{12}CO 2-1

^{13}CO 1-0

^{12}CO 1-0

"CO ice" means? at 4.67μ

Protoplanetary disks - ESO VLT

Class: based on slope of SED

1. 1R: richest \downarrow evolve
2. ...

arXiv: 1211.6750 NQC 1275 = Per A

H_2 (1-0) S(0)

$v=1, J=2 \rightarrow v=0, J=1$

(2-1) S(1)

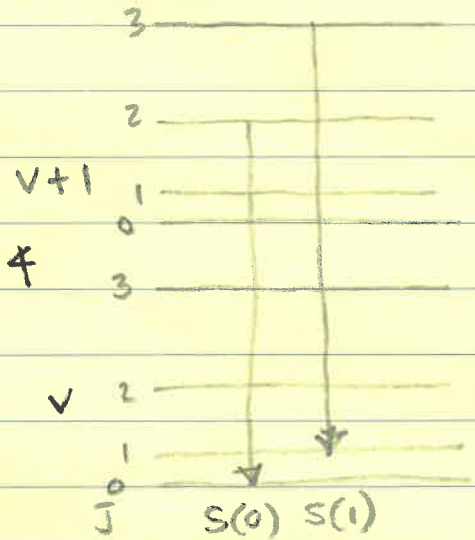
(3-2) S(2)

HI Br γ $n=7 \rightarrow n=4$

Brackett

He I $2p \ ^1P_1^o \rightarrow 2s \ ^1S_0$

H_2 (1-0) S(0) $2.122\mu\text{m}$



Electronic / vib / rot transitions

Molecule is approx stationary while electron undergoes transition



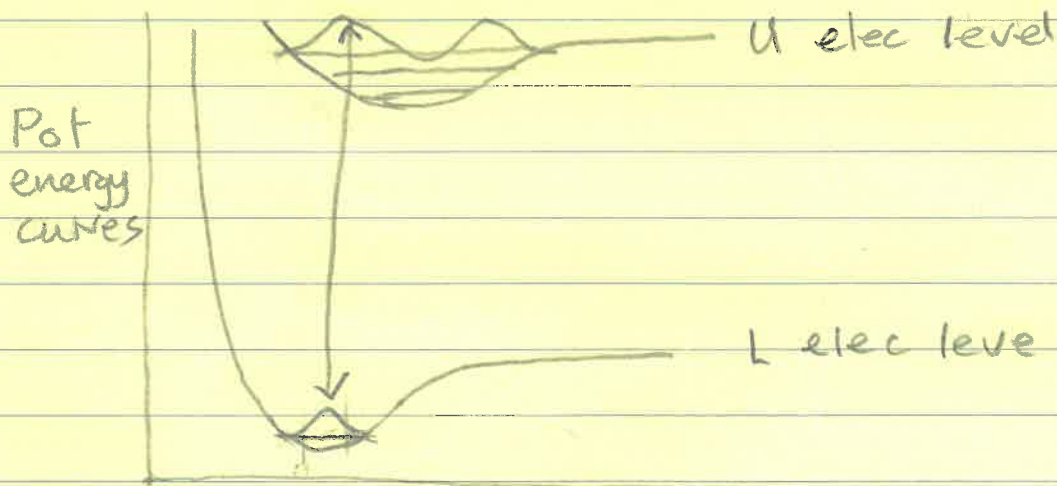
Franck-Condon principle for vib transition
 Hönl-London factor " rot "

Franck-Condon principle

In elec / vib / rot transition, vibrational probability is

$$\text{Prob}(v \leftrightarrow v') = |\langle v' | v \rangle|^2 = |\text{overlap of vib w.f.s}|^2$$

Note $\sum_{v'} |\langle v' | v \rangle|^2 = 1$



Hönl - London factors

In elec/vib/rot transition,
rotational probability is

$$\text{Prob} (J', K', S, \Lambda' \leftrightarrow J, K, S, \Lambda) = f(J', K', S, \Lambda' | J, K, S, \Lambda)$$

$s' = s$ Hönl - London factor

Note factors have stat. weight built in,
so factor is same for em & abs.
See notes hönl.ps.

Diatomic molecules: elec dipole selec rules

Hertzberg p. 240.

1. $\Delta \Lambda = 0, \pm 1$
 2. $\Delta J = 0, \pm 1$
but $J = 0 \not\leftrightarrow 0$
- } emitted photon
has unit ang mom
3. Total parity (elec & nuc) changes
because elec dipole phot has odd parity
 4. $\Delta S = 0$ because in $\langle n' \Lambda' | \vec{d} | n \Lambda \rangle$
elec spin dipole op \vec{d} indept of spin.
 5. If $\Lambda = 0 \leftrightarrow 0$, then $\Sigma^+ \leftrightarrow \Sigma^+$ or $\Sigma^- \leftrightarrow \Sigma^-$
 6. If same charge nuclei, then $\Lambda'_g \leftrightarrow \Lambda_u$

In addition,

Hund case (a)

7. $\Delta \Sigma = 0$ because elec spin unchanged
proj of elec spin along axis

$$\text{Hence } \Delta \underline{\Omega} = \Delta \Lambda = 0, \pm 1 \\ \equiv \Lambda + \Sigma$$

8. $\Delta J \neq 0$ if $\Omega = 0 \leftrightarrow 0$

Hund case (b)

9. $\Delta K = 0, \pm 1$

but $\Delta K \neq 0$ if $\Lambda = 0 \leftrightarrow 0$

Main branch has $\Delta J = \Delta K$ ($\vec{J} = \vec{K} + \vec{S}_{elec}$)

satellite branches $\Delta J \neq \Delta K$

Total (elec & nuc) parity = $\pm (-)^K$

For $\Lambda = 0$, \pm as Σ^\pm

For $\Lambda \neq 0$, each level is Λ -doubled, with even/odd parities, eg. Π^\pm .

Thus allowed transitions are

$$+ \leftrightarrow + \quad \Delta K = \pm 1$$

eg $\Sigma^+ \leftrightarrow \Sigma^+$, $\Pi^+ \leftrightarrow \Pi^+$, $\Sigma^+ \leftrightarrow \Pi^+$

$$+ \leftrightarrow - \quad \Delta K = 0$$

eg $\Pi^+ \leftrightarrow \Pi^-$, $\Sigma^+ \leftrightarrow \Sigma^-$.

Example: elec/vib/rot transitions of H₂

Allowed 1s - 2p transitions

"Lyman" band X ¹Σ_g⁺ 1s0 ↔ B ¹Σ_u⁺ 2pσ

"Werner" band ↔ C ¹Π_u⁺ 2pπ

arXiv: 0804.4761 Fig 7 p 12 astro-ph/0507581 Fig 3. p 30

Abs line from v=0 and J=0, 1, 2.

Forbidden transitions:

X ¹Σ_g⁺ 1s0 ↔ EF ¹Σ_g⁺ 2s0+2pσ g ↔ g

b ³Σ_u⁺ 2pσ

c ³Π_u⁺ 2pπ

a ³Σ_g⁺ 2s0

} S=0 ↔ 1

Allowed 2 - 2 transitions

Lower

Upper

EF ¹Σ_g⁺ 2s0+2pσ ↔ C ¹Π_u⁺ 2pπ

b ³Σ_u⁺ 2pσ

a ³Σ_g⁺ 2s0

c ³Π_u⁺ 2pπ

a ³Σ_g⁺ 2s0

Note

b ³Σ_u⁺ 2pσ ↔ c ³Π_u⁺ 2pπ forbidden u ↔ u.

But lowest c ³Π_u⁺ state has nowhere else to decay to. It is "metastable" and decays to b ³Σ_u⁺.

Here ΔS=0 rule beats g ↔ u rule

Notation

Lyman L(v_u - v_L) { P(J_L)
or B } R(J_L)

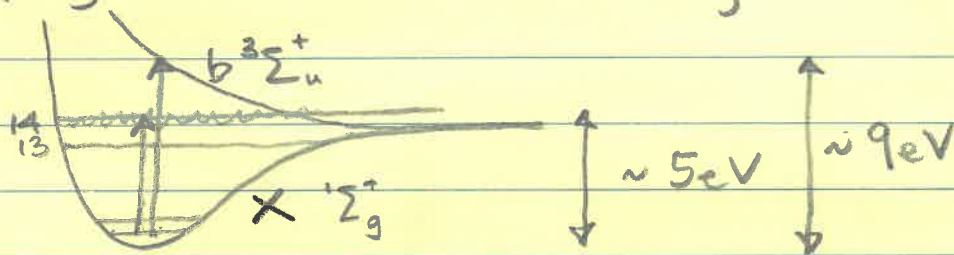
Werner W(v_u - v_L) {
or C }

Dissociation of H₂ binding energy 4.52 eV.

Various pathways



- (1) Collisional exc of v = 14 vib level of ground elec term X¹Σ_g⁺ unbound

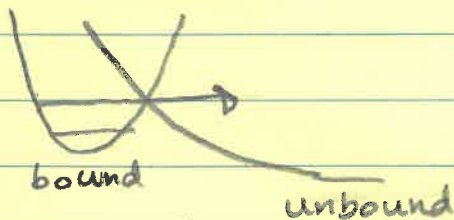


Unbound levels are broad ΔE Δt ~ ħ with Δt ~ 1 molecular vib time.

- (2) Collisional exc of b³Σ_u⁺ triplet, which is unbound.
- (3) UV photons excite singlet levels (eg B, c) which decay radiatively to unbound levels, eg X¹Σ_g⁺ v ≥ 14.

Predissociation

is transfer from bound elec/vib state to unbound elec/vib state



Association of H_2

Radiative association



is dipole forbidden, very slow.

So how does H_2 form?

(1a) $H + H \rightarrow H_2$ on surface of dust grain

(1b) Three-body recombination



Both these are reactions at "high" density.

(2) At $T \gtrsim 1500$ K, where H is partially ionized,



Why require hi T for H^- ? Need e for $H + e \rightarrow H^- + \gamma$

Primordial H_2

$n \gtrsim 10^4 \text{ cm}^{-3}$ for TE pop of rot levels.

HD provides additional coolant.



$n \gtrsim 10^8 \text{ cm}^{-3}$



Abel et al 1997

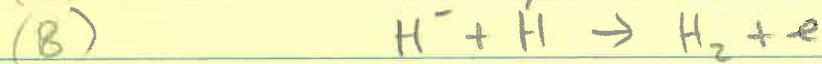
New Astron 2 181

Galli & Palla 98

AA 335 403

Glover & Abel 2008

MN 388 1627



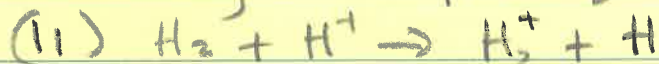
is dominant channel.

Alternative is

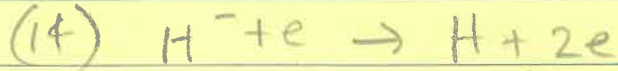
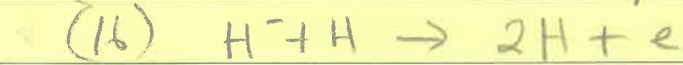
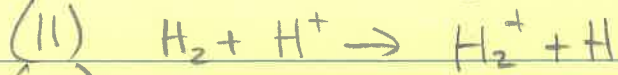
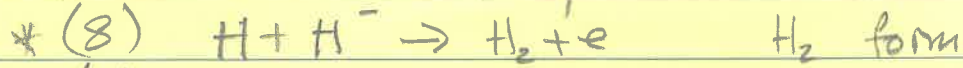
H_2^+ is more tightly bound than H^-



Cooling is $H + H_2$ exciting rovib.



Minimal model



All H^- goes to H_2 via (8)

H^- created via (7)

Does not affect e abundance - e is catalyst.