

Molecules

Molecules are found in cooler gas because of their ease of dissociation — e.g. cooler stellar atmospheres or cold ISM gas.
(100s of K) (2100s of K)

Diatomic molecules can exist up to $\sim 8000\text{K}$

Polyatomic must be $\leq 4000\text{K}$

Molecules have:

- electronic transitions — much harder to calculate!
no central force approximation!
- rotational & vibrational transitions associated
with the nuclei.

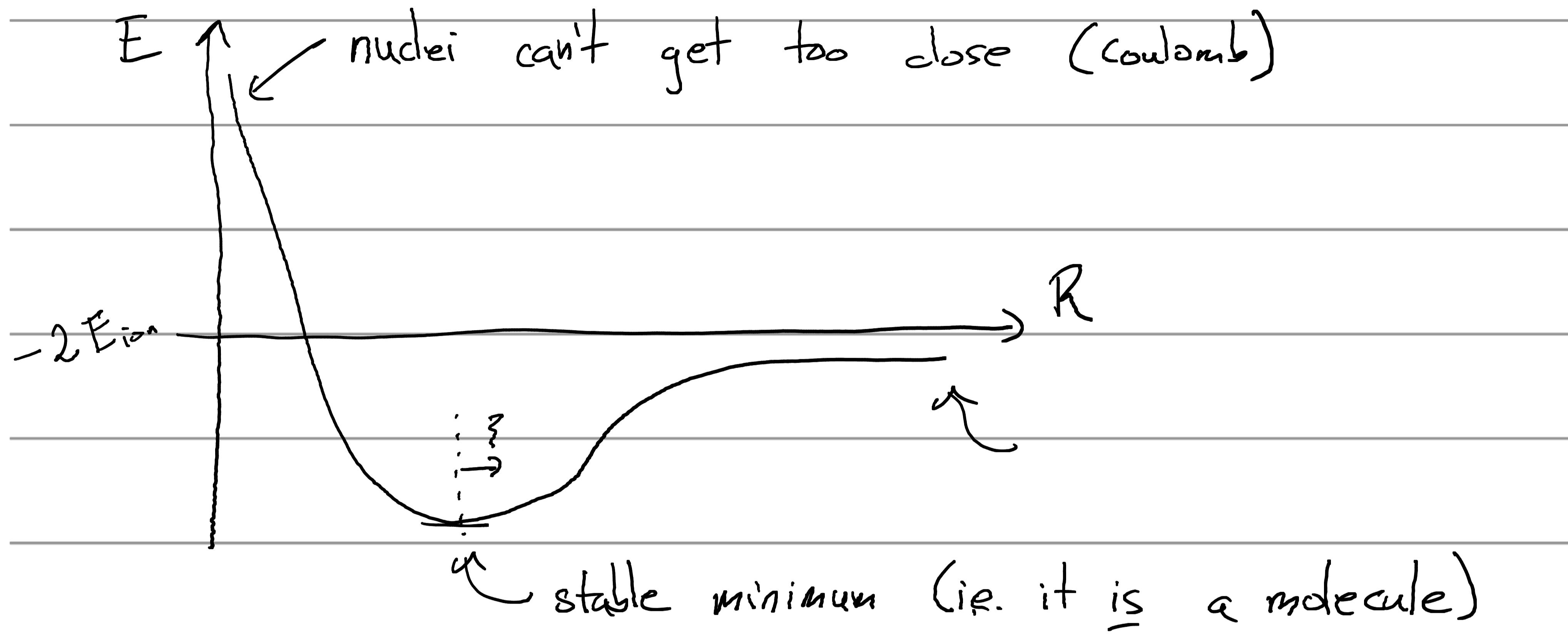
Born-Oppenheimer — separate electron w.f. from nuclei;

Also can separate rotational & vibrational modes

when electrons in ground state

Potential V as a function of separation of nuclei

must look like this. This potential set by e^- 's & nuclei.



For electronic energy levels:

$$\frac{p^2}{2m} \sim \frac{\hbar^2}{2m a^2} \quad \text{because } Dp \Delta x \sim p a^2 \hbar$$

Near minimum can approximate $E(R)$ as harmonic:

$$E \approx \frac{1}{2} M \omega^2 \zeta^2$$

Can estimate curvature of minimum by setting

$$E(\zeta = a) \sim \frac{\hbar^2}{2ma^2}$$

Then the vibrational energy levels will be of order:

$$E_{\text{vib}} \sim \hbar \omega \sim \left(\frac{\mu}{M} \right)^{1/2} \frac{\hbar^2}{2ma^2} \sim \left(\frac{\mu}{M} \right)^{1/2} E_{\text{elect}}$$

So generally much smaller.

The rotational energy can be written from QM as:

$$E_{\text{rot}} \sim \frac{\hbar^2 l(l+1)}{2I} \sim \frac{\hbar^2}{2Ma^2} \sim \frac{m}{M} E_{\text{elect}}$$

\uparrow moment of inertia

So:

$$E_{\text{elect}} : E_{\text{vib}} : E_{\text{rot}} \\ 1 : \left(\frac{m}{M} \right)^{1/2} : \frac{m}{M} \quad \frac{m}{M} \sim 10^{-4}$$

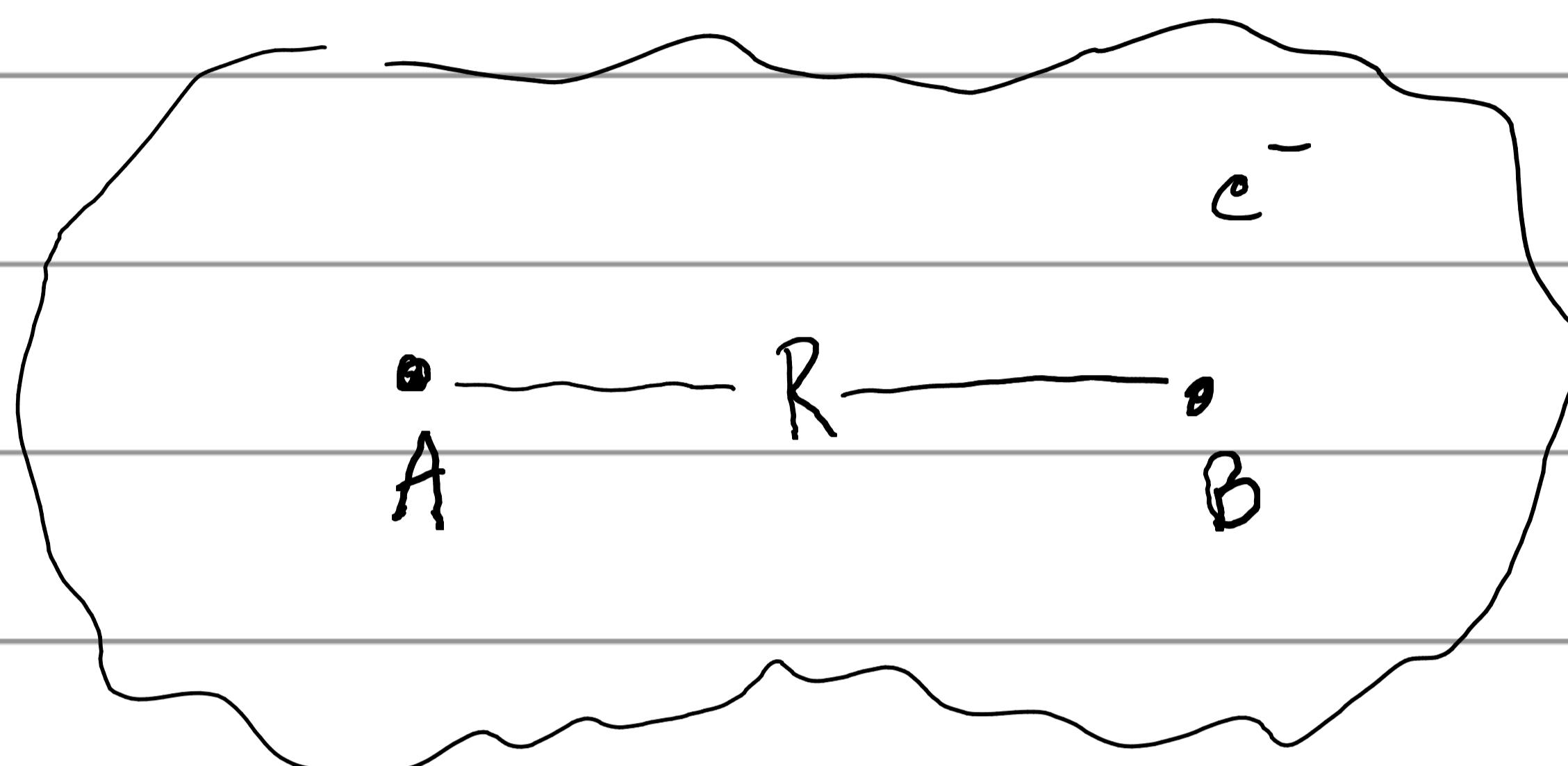
$$\text{eV} : 10^{-2} \text{eV} : 10^{-4} \text{eV}$$

optical

IR

radio

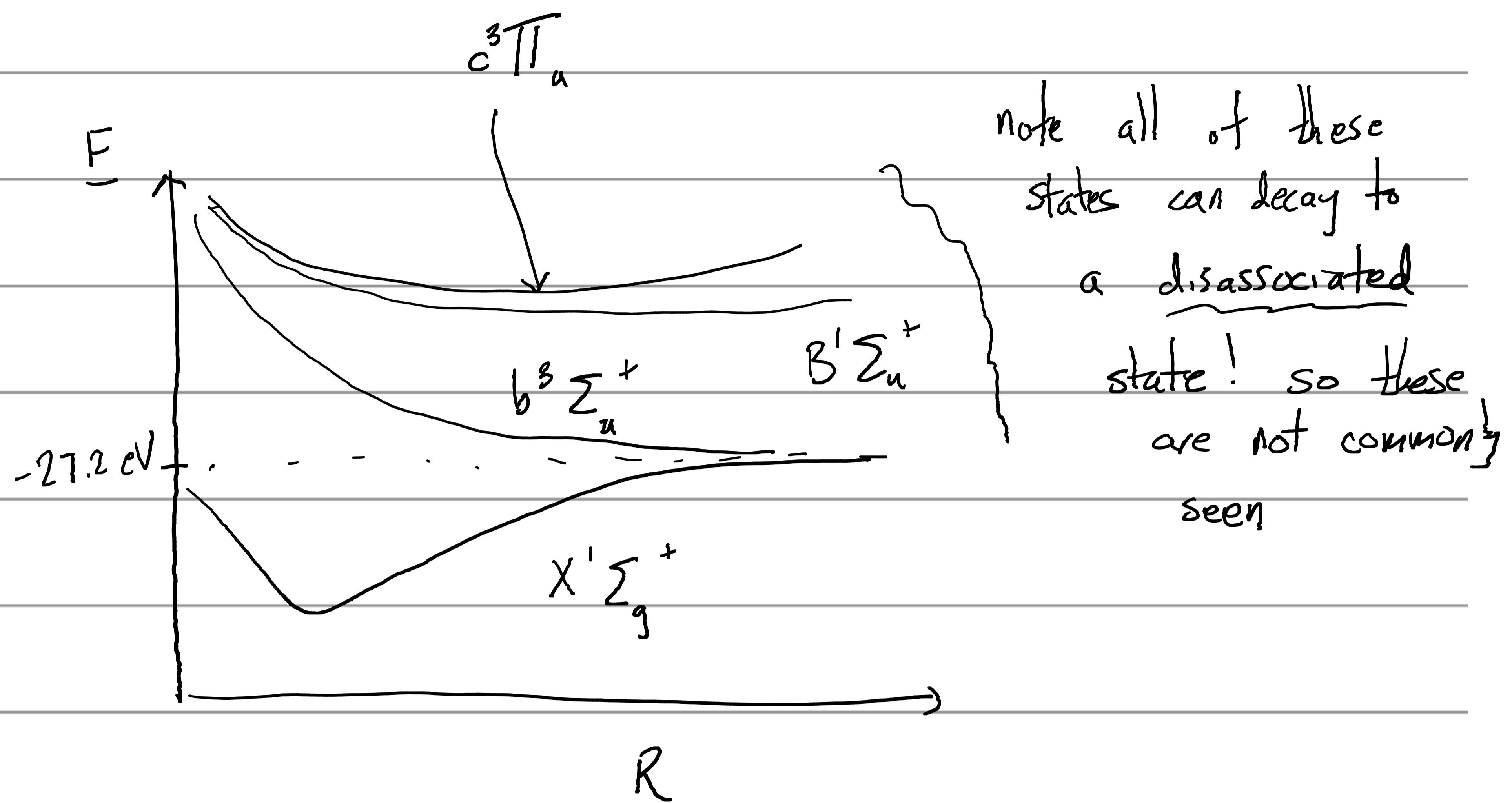
Born-Oppenheimer recognizes that electrons move much faster than nuclei (essential to above hierarchy) and therefore they adjust quickly to changing \vec{R}



This motivates the separation:-

$$\Psi(\vec{R}_A, \vec{R}_B, \vec{r}_e) = \underbrace{\psi_e(\vec{r}_e; R)}_{\text{electronic levels}} \underbrace{\psi_v(\vec{R}_A, \vec{R}_B)}_{\text{vibrational + rotational levels}}$$

E.g. for molecular H:



$\Sigma, \Pi, \Delta, \dots$ for angular momentum on nuclear axis
(which is conserved)

X = ground

$A \dots$ = higher state w/ same spin multiplicity as X

$a \dots$ = .. " different "

g = symmetric
 u = antisymmetric

} for homonuclear diatomics

But: many exceptions ...

Many important molecules have $\Lambda > 0$ in the ground state. Note that $\Lambda > 0$ can be + or -, because it is a signed quantity, and in a heteronuclear atom this will lead to a level splitting ("lambda doubling").

In a few high-Z molecules there are multiple electrons in open shells and that leads to electronic states that do not exceed dissociation energy. Very complicated spectra and typically a strong source of opacity in atmosphere. TiO, FeH, VO, etc.

In cases like H₂ or CO, the excited electronic states can lead to emission in cases they are populated non-thermally by energetic processes. In places like molecular clouds, they are only seen in absorption.

The remaining nuclear part of the wave function describes its translation, rotation, & vibration.

Translation won't matter, and for two nuclei we can work in the reduced frame and treat it like a central force problem.

Then the angular momentum states are:

$$E_r = \frac{\hbar^2}{2\mu R^2} J(J+1) \quad \mu = \frac{M_A M_B}{M_A + M_B}$$

So there are J, M_J states. Pretty good approximation if $R = \text{constant}$ ("rigid") $\rightarrow R \& L$ describe lowest order corrections to that.

The vibration states are:

$$E_v = \hbar \omega \left(v + \frac{1}{2}\right)$$

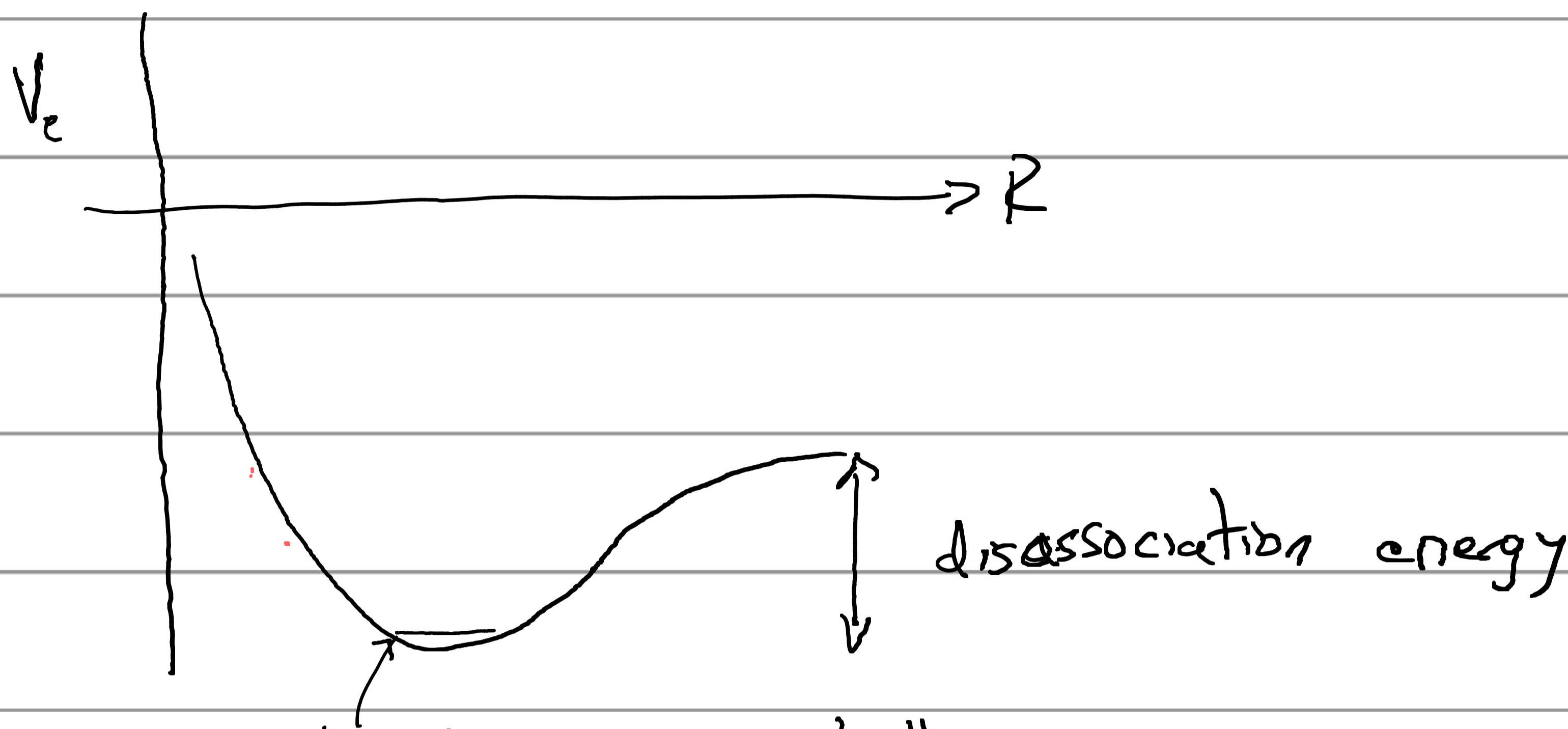
$$v = 0, 1, \dots$$

because this is like a spring

$$\omega \propto \mu^{-1/2}$$

The vibration degree of freedom has an important effect on molecules, with observable effects in the ISM.

If we consider the electronic potential:



lowest energy is actually

$$V_{\min}(R) + \frac{1}{2} \hbar \omega$$

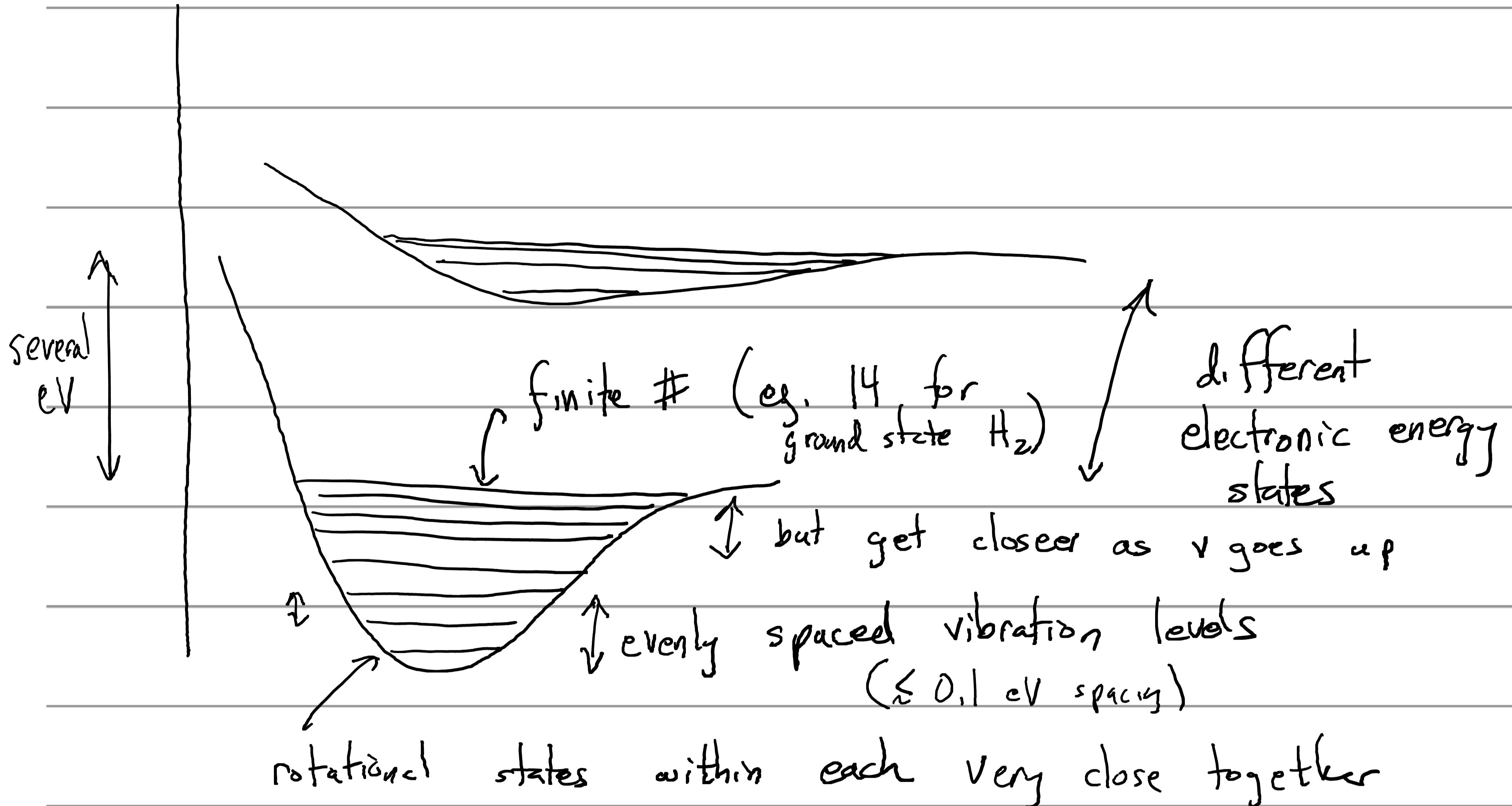
Slightly lowers dissociation energy. And $\omega \propto \mu^{-\frac{1}{2}}$
so the higher the mass the lower the effect, so the more stable the molecule.

E.g. take HD vs. H₂

$$\mu_{HD} = \frac{2}{3} M_H \quad \mu_{H_2} = \frac{1}{2} M_H \quad \rightarrow \quad \frac{\omega_{HD}}{\omega_{H_2}} = \frac{\sqrt{3}}{2}$$

Quantitatively, $\Delta E_{HD-H_2}/k \sim 400 \text{ K}$; so at low T HD quite favored. $HD/H_2 \sim 1000^{\frac{D}{H}}$ "deuterium fractionation"

Vibrational-Rotational Energy Levels



$$E_{vJ} = \hbar \omega_e \left(v + \frac{1}{2}\right) + \beta_e J(J+1) - \hbar \omega_e \chi_e \left(v + \frac{1}{2}\right)^2 - D_e J^2(J+1)^2 - \alpha_e \left(v + \frac{1}{2}\right) J(J+1)$$

Boltzmann says

$$\frac{P(J)}{P(0)} = \frac{g_J}{g_0} e^{-E_J/kT}$$

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

$$g_J = 2J+1 \text{ for heteronuclear}$$

→ for homonuclear the nuclear spin state comes in

Typically $kT \gg E_J$, so higher J states more populated than $J=0$ state.

Vibrational states have $J=1$ and E_v large relative to molecular cloud temperatures, so are considerably less populated.

Rotational Transition Selection Rules

Dipole transitions require a permanent dipole moment relative to the center of mass.

So homonuclear diatomics do not have dipole transitions, just quadrupole. This is one reason H_2 is weak; the other reason is that $\hbar^2/2\mu R^2$ is high (because μ is low)

For diatomic molecules in Σ -type electronic state

$$\Delta J = \pm 1$$

$$\Delta E_{\text{rot}} = \frac{\hbar^2}{2\mu R^2} [J''(J''+1) - J'''(J'''+1)]$$

$$= \frac{\hbar^2}{2\mu R^2} [(J''+1)(J''+2) - J'''(J'''+1)] = \frac{\hbar^2}{\mu R^2} J''$$

in
constant
spacing

Most important instance is CO. Dissociation energy is 11.1 eV → very stable! This means CO tends to lock up all of either C or O. This has a major consequence for ^{cool} stars → mostly there are fewer C atoms than O. So, all C ends up in CO, and the remaining O forms molecules like TiO, which produces very characteristic absorption in most cool stars. A rarer type of star has more C than O, and this causes a dramatic change in its spectrum from oxide-type absorption to CN, C₂ absorption.

J 1 - 0	2.60 mm	$\frac{1}{2}$	$A \sim 10^{-7} \text{ s}^{-1}$
2 - 1	1.30 mm	$\frac{1}{2}$	(weak dipole)
3 - 2	0.87 mm	$\frac{1}{2}$	
		$\frac{1}{4}$	
		:	

In galaxies, CO is an excellent tracer of molecular clouds, often used as a proxy for H₂. Complicated by optical thickness. Higher excitation lines & isotopes help.

C¹³O¹⁶ or C¹²O¹⁸ are much less abundant and have sufficiently different $\chi^2/2\mu R^2$ to be easily separated.

$$\mu = \frac{M_c M_o}{M_c + M_o} = \frac{(12)(16)}{12 + 16} m_p \sim 6.9 m_p$$

vs. (e.g. $C^{13}O^{16}$) $\frac{(13)(16)}{13 + 16} m_p \sim 7.2 m_p$

So $\frac{\Delta\lambda}{\lambda} \sim \frac{\Delta\mu}{\mu} \sim 0.05 \rightarrow$ big line shift!

Note for H_2 , there is a lot of it, and particularly in warm environments it can be observed. But since it will emit as electric quadrupole its selection rules are:

$$\Delta J = \pm 2$$

And because it is much lighter than CO , it is shorter wavelength

$$J 2-0 : 28 \mu m \quad A \sim 10^{-11} s^{-1}$$

Vibrational Transitions aka rotation-vibration transitions

Selection rule $\Delta v = \pm 1$ for harmonic (and these

$$\hookrightarrow \Delta E_v = \hbar \omega$$

transitions are strong in all cases)

The energy change is \gg rotation so natural to expect a change in rotational state, and they obey selection rules:

$$\Delta J = \pm 1 \quad (\text{for electric dipole in } \Sigma \text{ state})$$

(or, for non Σ states you can get $\Delta J = 0$ if dipole moment is changed)

Also $\left. \frac{d(d)}{dr} \right|_{r=r_0} \neq 0$ under excitation

↑ this excludes electric dipole transitions for homonuclear diatomic molecules

Spectrum has $\Delta v = \pm 1$ but $\Delta J = \pm 1$ as well:

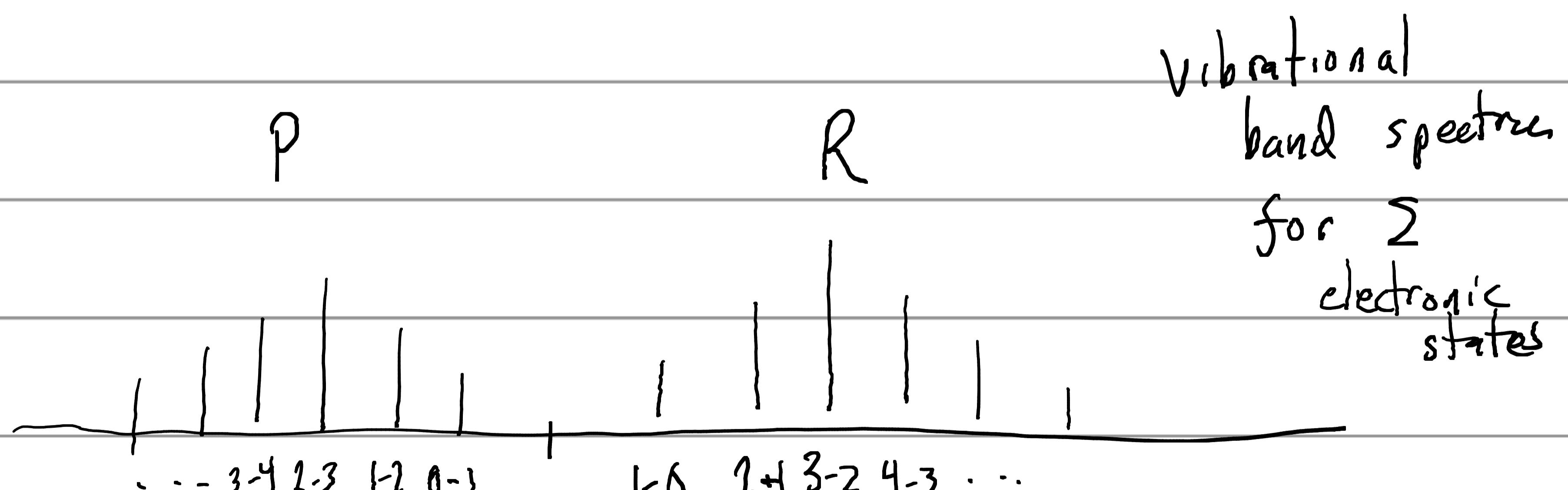
R-branch is $\Delta J = +1$ $J' = J'' + 1$

$$\Delta E_{vR} = \hbar\omega + J'(J'+1) \frac{\hbar^2}{2\mu R'^2} - J''(J''+1) \frac{\hbar^2}{2\mu R''^2}$$

$$\approx \hbar\omega + \frac{\hbar^2}{\mu R^2} J' \quad J' = 1, 2, 3, \dots$$

P-Branch is $\Delta J = -1$

$$\Delta E_{vP} \approx \hbar\omega - \frac{\hbar^2}{\mu R^2} J''$$



$\hbar\omega$

— ΔE —————

For non- Σ electronic states $\Delta J=0$ allowed, leading to a Q-branch near thus.

Again, isotopic effects are detectable, but this time $\omega \propto (\mu)^{-1/2}$ so are somewhat weaker.

And H₂ again must obey $\Delta v = \pm 1$ but $\Delta J=0, \pm 2$
(not O-O)

The existence of $\Delta J=0$ leads to a "Q" branch,

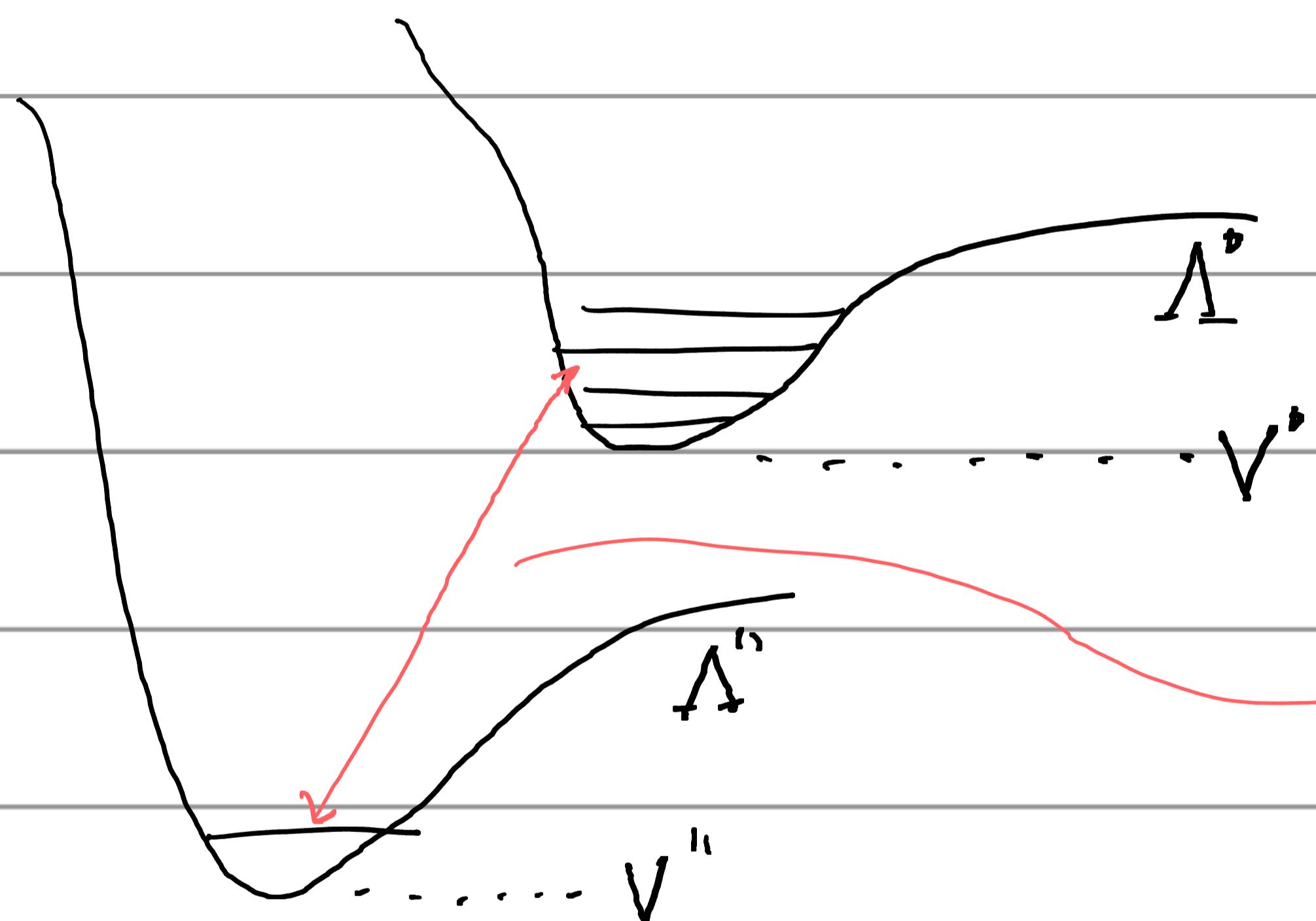
P branch \rightarrow "S" } different naming for H₂
R branch \rightarrow "O"

H₂ can be found in planetary nebulae, merging galaxies

Electronic Transitions

Most complicated type of transition! involves change in electronic state but will also involve rotation + vibration

Mostly only need to worry about electric dipole. That's because higher energy states can dissociate so only strong transitions will be observable.



Let's consider
these transitions

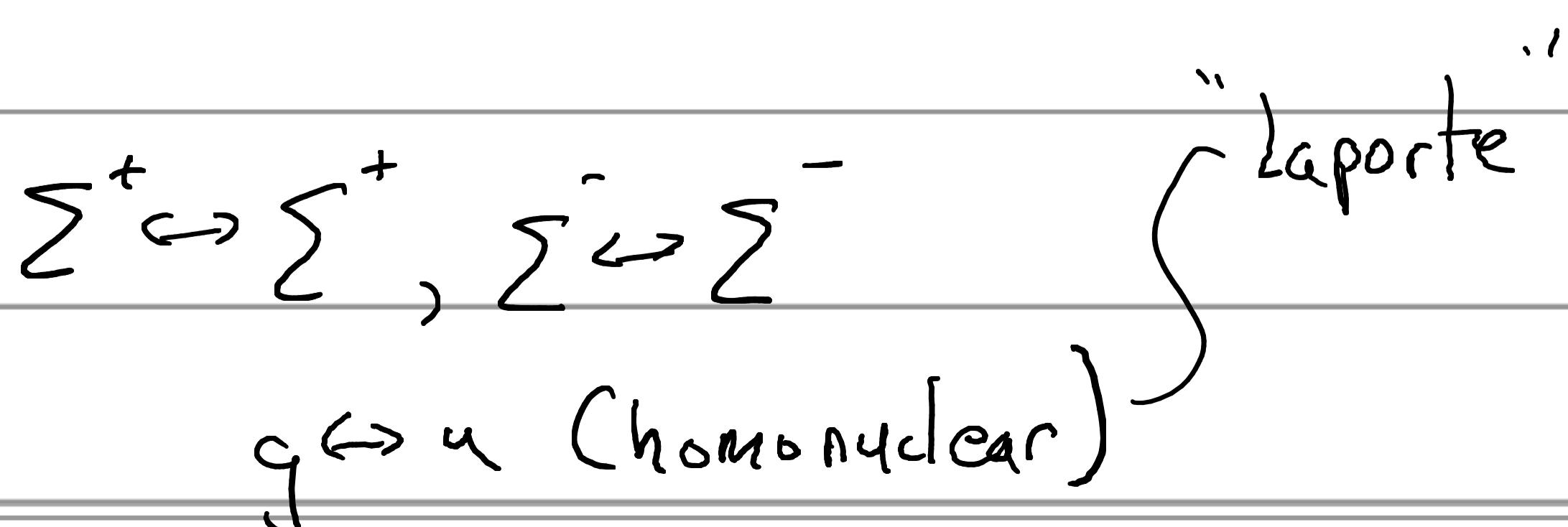
$$\Delta J = \pm 1 \text{ for } A = 0-0$$

$$\Delta J = 0, \pm 1 \text{ (no } 0-0\text{) for after } \Delta A$$

any Δv

$$\Delta S = 0$$

$$\Delta A = 0, \pm 1$$



Electronic transitions are referred to as bands because of the dense series of rotational & vibrational transitions.

$$E_{cvJ} = V_e + \underbrace{\gamma_e \frac{t^2}{\hbar} J^2}_{V_{oe}} + \alpha_e \frac{t}{\hbar} J(J+1) + \frac{\hbar \omega_e}{2} (v + \frac{1}{2})$$

$$\Delta E = E_{e'v'J'} - E_{e''v''J''}$$

$$= (V_{oe''} - V_{oe''''}) + V''\omega_{e''} - V'''\omega_{e''''} + H(J'')$$

Where :

$$H = \alpha_e \frac{t}{\hbar} J''(J''+1) - \alpha_{e''''} \frac{t}{\hbar} J'''(J'''+1)$$

$$P \quad J'' = J''' - 1$$

$$\left\{ \begin{aligned} & \hbar J''' [\alpha_{e''''}(J'''-1) - \alpha_{e''''} J''(J''+1)] \\ & \qquad \qquad \qquad \end{aligned} \right.$$

$$Q \quad J'' = \overline{J}'' + 1$$

$$H(J'') = \left\{ \begin{aligned} & \hbar \overline{J}'' (\overline{J}''+1) [\alpha_{e''''} - \alpha_{e''''}] \\ & \hbar (\overline{J}''+1) [\alpha_{e''''}(\overline{J}''+2) - \alpha_{e''''} \overline{J}''] \end{aligned} \right.$$

$$R \quad \overline{J}'' = \overline{J}'' + 1$$

$\Delta V_o = V_{oe^*} - V_{oe^{**}}$ is the dominant term

setting frequency \rightarrow so will
be cV-scale

Vibrational transition $v'' - v'$ leads to a progression.

The rotational structure at a given electronic & vibrational transition is a band

Consider :

