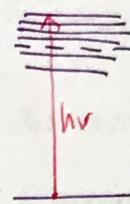


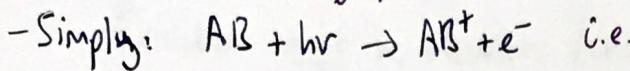
Photocluster (7+P)

Photoionisation

you would absorb > 1 photon per multiple ionization

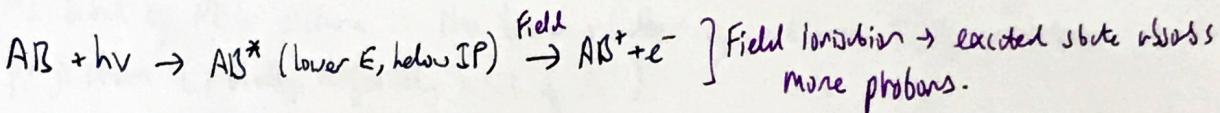
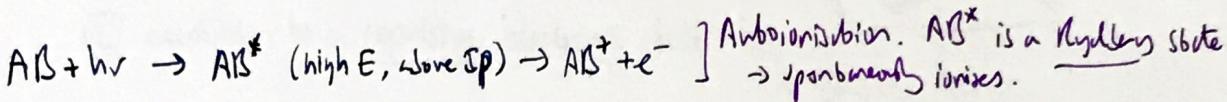
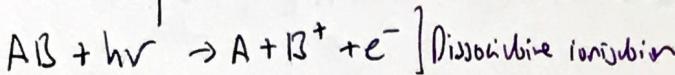


not quantised \therefore unbound
continuum states above IP



Ionisation Limit (IP)

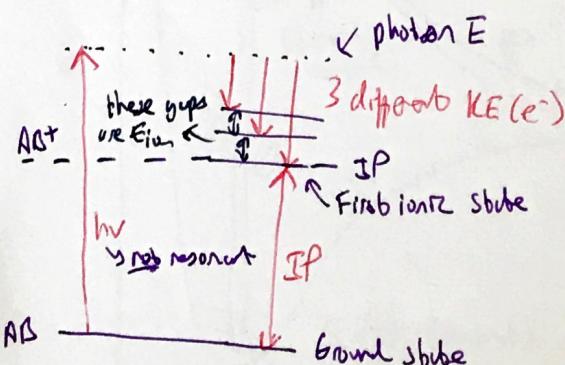
- Other related processes:



- hv doesn't have to be resonant, as the final states are unbound, \therefore not quantised.

\rightarrow or, it has to be resonant with a continuum!

- Energy has to be conserved: $hv = I + E_{\text{ion}} + KE(e^-) + KE(AB^+)$ $\approx 0 \because \text{ion is huge.}$



$$\text{i.e. } KE(e^-) = hv - I - E_{\text{ion}}$$

measure this with a spectrometer

know this, from laser

constant

confirms this!

Koopmans Theorem: $E(\text{Orbital } E) = -I - E_{\text{ion}}$

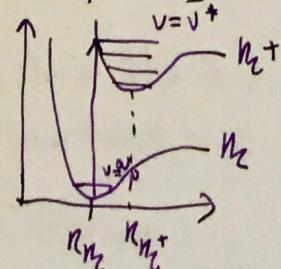
vibration levels of AB^+

In general, you measure excited vibrational states \because bond length following ionization changes a lot! e.g. $N_2 \rightarrow N_2^+ + e^- \rightarrow$ F.L. overlap!

\rightarrow Then you'd see a long progression (bonding e^- removed)

\rightarrow short progressions if you remove a non or anti bonding e^- .

\rightarrow See Stuart's notes on this, and the past paper problem we did at the start of MT.



Photodissociation

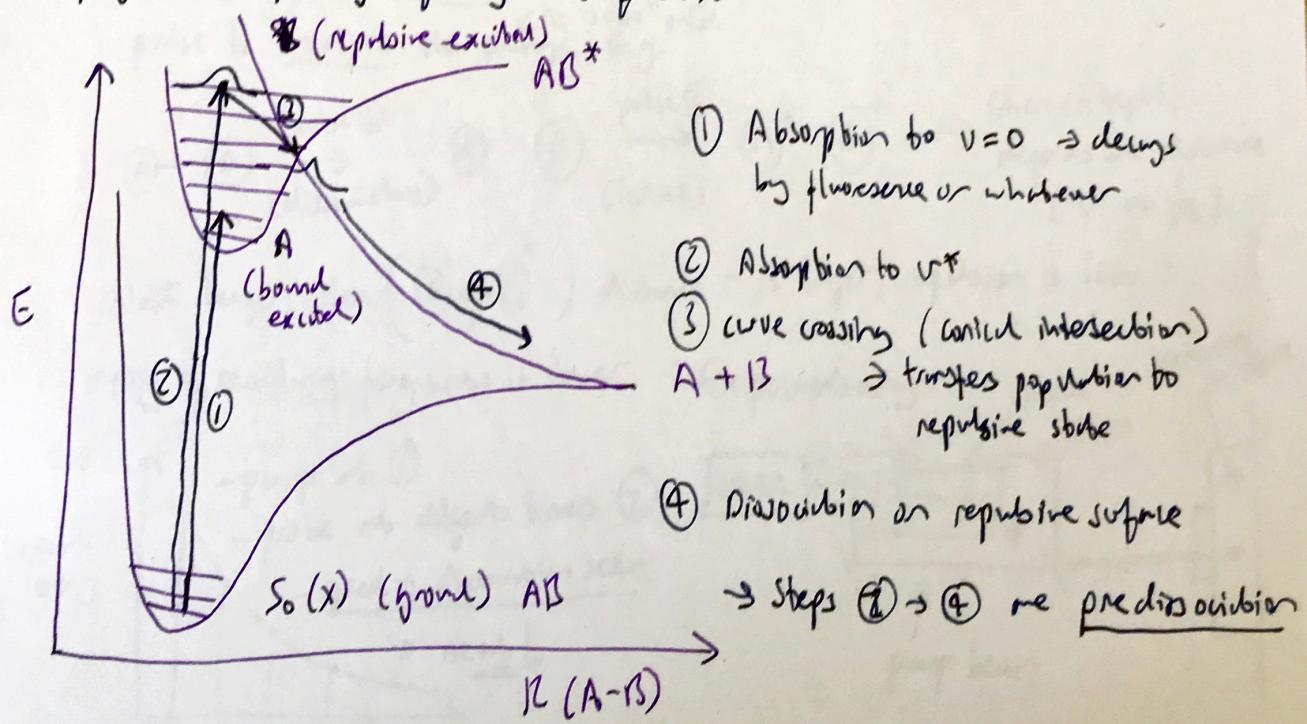
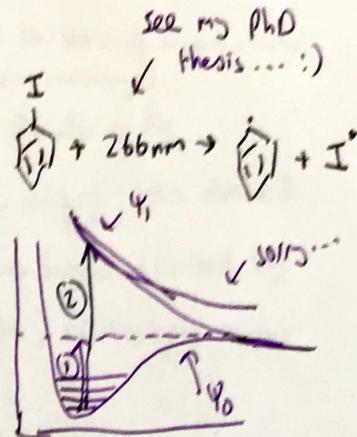
- Break bonds with photons. My favorite example:

- Excitation must be electronic (unless it's weird).

① never going to work $\because \Delta V = +100$ or something silly

② excitation to a repulsive electronic state

This kind of PES picture is the bread + butter of well over 50% of modern phys chem (probably definitely a lot of it!).



Lifewidth + lifetime resolution

- Spectral lines have a finite width ΔE ($\Delta\lambda$, $\Delta\nu$). This is a measure of the uncertainty in E , and is related to uncertainty in t by

$$\Delta E \Delta t \approx \frac{\hbar}{2} \quad (\text{depends a lot on lineshape})$$

$\therefore \Delta E$ gives a measure of lifetime of the absorbed excited state. Broad lines \Rightarrow short lifetime and vice-versa.

Ultrashort Chemistry \rightarrow my entire PhD...! (I can send the thesis if anyone wants some led time reading).

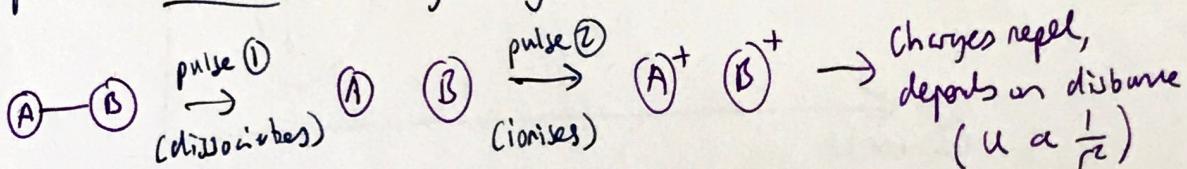
- linewidths are related to excited state lifetimes by $\Delta E \Delta t \approx \frac{h}{\lambda}$
- however, for processes that are actually fast (i.e. ~ 100 fs), this doesn't help because electronics cannot measure the ultrashort times. (limited by how fast electrons in wires move! The best (i.e. 8000k) oscilloscopes might get you 10 ps time resolution).

\rightarrow solution: measure it all using optical techniques.

Pump-Probe Chemistry

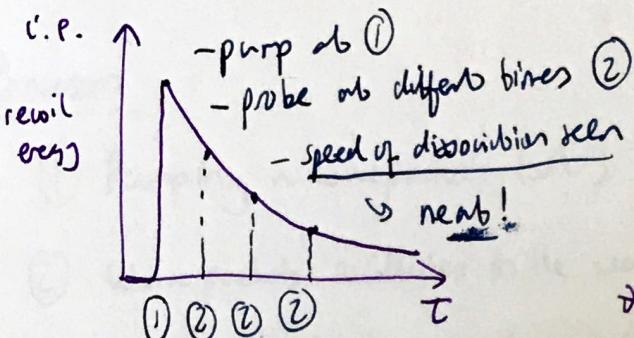
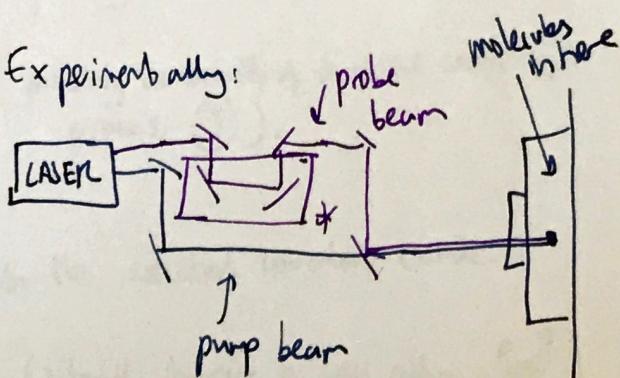
the "pump" pulse $\xrightarrow{\text{time } T}$ by delaying 2 pulses.

- use one pulse to initiate some change, then wait a bit, then use another pulse to measure the change. E.g.:



Wait longer, then $(A^+ \leftrightarrow B^+)$ distance r is larger, repulsion is less. \therefore energy of repelling fragments is lower.

Experimentally:

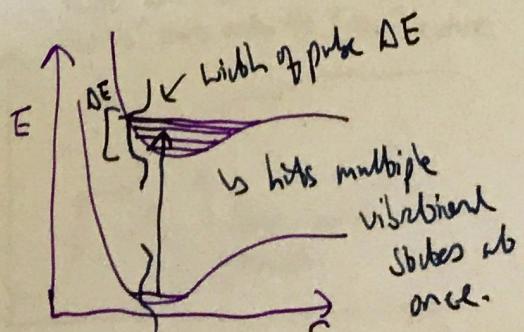


* mirrors move so that the probe pulse travels further \therefore arrives later.

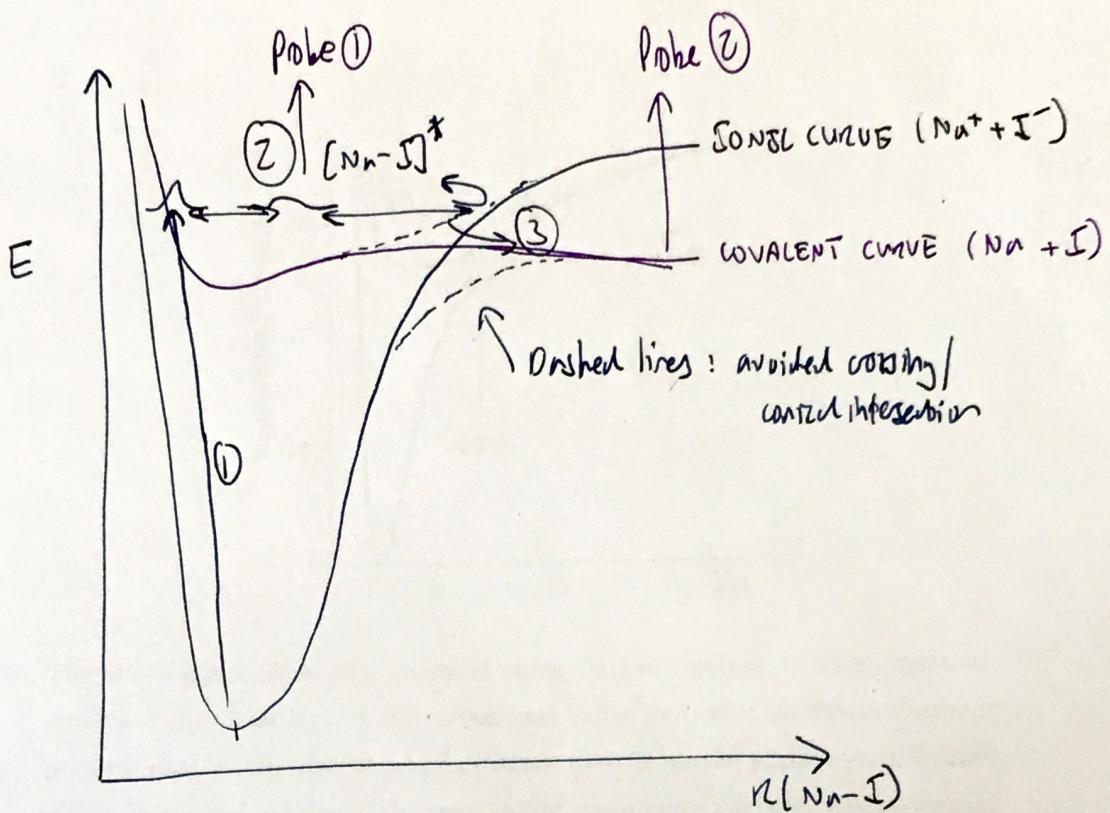
Wavepackets

- Ultrashort laser pulses have a range of different colors of light in them (ΔE uncertainty).
- So they hit several different states at once, depending on how wide ΔE is.

$$\Psi(x, b) = \sum_n a_n \Psi_n e^{-i \omega_n t}$$



Sodium iodide example



Probe ①: fluorescence from $[\text{Na}-\text{I}]^*$ (probing oscillation, process ②)

Probe ②: fluorescence from $[\text{Na}]$ (probing the result of avoided crossing, process ③).

Processes

- ① Pumping a wavepacket (α) onto the excited covalent curve.
- ② Wave packet oscillates in the well (literally imagine a ball rolling )
- ③ Avoided crossing onto the covalent curve. \rightarrow populates/generates $[\text{Na}]$

Measurements

