P.E. Curves & Electronic States

If we consider the H₂ molecule and its $1\sigma_g^2$ configuration:

Formation of bonding and anti-bonding MOs from the AOs, having $\sigma_g$ and $\sigma_u$ symmetry, respectively (symmetric or anti-symmetric w.r.t. to inversion and reflection $\perp$ to the axis).

When considered in the context of a potential energy diagram, the bonding (bound), anti-bonding (repulsive) and non-bonding (dissociative) MO’s can be pictured as:
Potential Energy Curves

So far, we have only considered the potential energy curve of the ground state of a molecule - but in fact, the potential energy curves of the excited states lend much to the understanding of molecular structure.

Pictured to the left are the molecular potential energy curves for the ground state (1σ) and excited states (2σ and higher) of the H$_2^+$ ion as a function of internuclear distance.

- The ground state is referred to as a **bound state** (resembles the Morse potential type curves).

- Excited states are normally referred to as **repulsive** states, though some can act as bound states (3σ above).
**C₂ Molecule**

Important in astrophysics, and observed in the emission spectra of comets and absorption spectra of stellar atmospheres, the C₂ molecule has a ground configuration: $(\sigma_1s)^2 (\sigma^*_1s)^2 (\sigma_2s)^2 (\sigma^*_2s)^2 (\pi_1^*)^2 (\pi_2^*)^4$, has a $X^1\Sigma^+_g$ ground state, and a variety of low-lying excited electronic states (low lying states involving promotion of e- from the $\pi_1^*2p$ or $\sigma^*_u2s$ orbital to the $\sigma_1g2p$ orbital, are allowed by Hund’s case (a) selection rules).
The electronic transitions of \( \text{C}_2 \) are observed in a variety of astral phenomena, but also in a number of discharge and emission processes in the laboratory:

There are two principal band systems of \( \text{C}_2 \) which are observed in the optical in the spectra of comets. These are the Swan or \( \text{d}^3\Sigma_g^- - \text{a}^3\Pi_u \) system and the Phillips or \( \text{A}^1\Pi_g - \text{X}^1\Sigma_g^+ \) system.

The Swan system is dominant in the green, orange and red region of the spectrum, while the Phillips is important in the near-IR and IR regions. Cochran et al., in their studies of the tail of Comet 122P/de Vico, found that the \( \Delta \nu = +1, 0 \) and \(-1\) bands of the Swan system had rotational lines with very high \( J \)-values, up to \( J=109! \) See: *Icarus, 2002, 157, 297-308.*
**Vibrational Coarse Structure**

The molecule may vibrate and rotate in excited electronic states in a similar manner to the ground state. The total term value $S$, for a molecule with an electronic term value, $T$, corresponding to an electronic transition between equilibrium configurations with vibrational and rotational term values $G(\nu)$ and $F(J)$, is written as:

$$S = T + G(\nu) + F(J)$$

We will focus first on the anharmonic vibrational term:

$$G(\nu) = \omega_e (\nu + \frac{1}{2}) - \omega_e x_e (\nu + \frac{1}{2})^2 + \omega_e y_e (\nu + \frac{1}{2})^3 + ...$$

In many electronic experiments, the spectra will be too broad to resolve any **vibrational coarse structure** (e.g., experiments in liquid phase, etc.), but under the right conditions, it may be possible to observe the variation of $\omega_e$, $\omega_e x_e$, $\omega_e y_e$, etc. between different electronic states.

For instance, in the absorption spectrum of benzene (arising predominantly from $\pi \rightarrow \pi^*$ transitions from C=C bonds), typically only a broad peak is observed. Under certain circumstances, the **vibrational structure** can be resolved (e.g., gas phase, slow scans)
Vibrational Coarse Structure for O$_2$

This means that each electronic level has a stack of vibrational levels associated with it - depending on the shape of the p.e. curve, there may be a large series of vibrational energy levels (deep minimum), very few vibrational levels (shallow minimum), or no vibrational levels (no minimum).
Above is a picture of the vibrational energy levels associated with two electronic states, along with allowed electronic transitions. The vibrational energy levels in the upper and lower states are labelled $v'$ and $v''$, respectively.

Vibrational transitions which accompany the electronic transitions are called vibronic transitions (if accompanied by rotational transitions, called rovibronic transitions).

The vibronic transitions give rise to bands in the spectrum, and a set of bands associated with a single electronic transition is the electronic band system.

Progressions involve sets of vibronic transitions with a common upper or lower level, whereas sequences are groups of vibronic transitions with the same $\Delta v$. 
Perhaps surprisingly (after all of the selection rules we have discussed), there is no restriction on values of $\Delta \nu$, though as we shall see, some of the intensities of the transitions are limited (due to the Franck-Condon principle).

As well, a necessity for a transition to occur is that the initial state of the transition have a high enough population for the transition to be observed: thus, any population of a starting level $v''$ is related to the $v'' = 0$ level by

$$\frac{N_{v''}}{N_0} = \exp - \left[(G(v'') - G(0)) \frac{hc}{kT}\right]$$

which implies that the $v'' = 0$ progression will be prominent in the absorption spectrum at standard temperatures.

A progression with $v'' = 1$ may also be observed in absorption, but only with a wavenumber low enough for this energy state to be populated. A famous example is the $B^3\Pi_{0''} - X^1\Sigma_g^+$ transition in I$_2$, which absorbs in the visible region, in which bands from $v'' = 0, 1$ and 2 progressions are observed.
Franck-Condon Principle

Franck, in 1925, developed the classical idea of what was to become the **Franck-Condon principle**: “An electronic transition is so fast compared to nuclear motion that the nuclei have nearly the same position and momentum after the transition as before”

Consider electronic transitions (absorption process) from a lower ground state to an excited electronic state where (a) $r_e' > r_e''$ and (b) $r_e' \approx r_e''$.

(1) If the electronic transition is very fast, the nuclei have the **same position** before and after the transition, then points A and B lie along a vertical line (if $r$ remains constant during a transition, denoted a **vertical transition**).

(2) The nuclei must also have the **same velocity** before and after the transition, so point A goes to point B, the latter of which is the classical turning point of the vibration (i.e., velocity is zero).

**in (a):** C-A: unlikely, since large change in $r$ (position); D-A: unlikely, since nuclei in motion at point D

**in (b):** B-A: likely, no vibrational energy in upper state; C-A unlikely, nuclear veloc. increased, $KE = BC$ distance
Condon treated these ideas quantum mechanically in 1928. The intensity of a vibronic transition is proportional to the square of the transition moment $R_{ev}$:

$$R_{ev} = \int \psi'^*_{ev} \mu \psi''_{ev} d\tau_{ev}$$

where $\mu$ is the electric dipole moment operator and $\psi_{ev}$ are the vibronic wavefunctions of the upper and lower states. Integration is over both vibrational and electronic coordinates. Assuming the Born-Oppenheimer approximation is valid, $\psi_{ev}$ can be factorized:

$$R_{ev} = \int \int \psi'^*_{e} \psi'^*_{v} \mu \psi''_{e} \psi''_{v} d\tau_{e} dr$$

If we integrate over electron coordinates, $\tau_{e}$, we have

$$R_{ev} = \int \psi'^*_{v} \psi''_{v} R_{e} d\tau_{e} dr$$

where $r$ is internuclear distance $R_{e}$ is the electronic transition moment which is written as:

$$R_{e} = \int \psi'^*_{e} \mu \psi''_{e} d\tau_{e}$$

Since the nuclei are regarded as stationary with regard to the fast moving electrons, $R_{e}$ can be treated separately:

$$R_{ev} = R_{e} \int \psi'^*_{v} \psi''_{v} dr$$

where the integral above is the vibrational overlap integral which can be evaluated to give the Franck-Condon factor ($r$ is assumed to remain constant for this to be a constant factor)
In the quantum mechanical picture, the classical turning point of a vibration (nuclear velocities zero) is replaced by a maximum or minimum in $\psi_v$ near its turning point.

Here, the maximum of the $v' = 4$ transition near to the classical turning point is vertically directly above that of the $v'' = 0$ vibrational wavefunction. The maximum contribution of the overlap integral is indicated by the solid line, though the dashed lines indicate the limits of $r$ containing appreciable contributions to transition intensity.

**Progressions:**
(a) When $r_e' \approx r_e''$, intensity maximum in the electronic spectrum occurs for $v' = 0$. (b) For $r_e' > r_e''$, as in the 4-0 case pictured above, the maximum in the $v'' = 0$ progression occurs at $v' = 4$. (c) If $r_e' \gg r_e''$, there is intensity involving the continuum of vibrational levels above the dissociation limit. The intensity maximum occurs at some high value of $v'$ and the individual lines “blur” into one another towards high frequency.
Franck-Condon Principle, 4
Summarizing the classical and quantum mechanical points of view:

Classical (Franck):

For the vertical transition, the nuclei are at approximately the same position (i.e., \( r_e \) or nuclear coordinates). The nucleus is stationary in the minimum of the ground state, and at the turning points of the excited states.

Quantum (Condon):

The molecule undergoes a transition to the upper vibrational state that most closely resembles the vibrational ground state of the lower electronic state (greatest overlap integral of vibrational states - most similar)
The various types of vibronic progressions and sequences suggest that a method of combination differences can be used to obtain the separations of the vibrational levels from the observed wavenumbers: specifically, we would like to obtain $\omega_e$, $\omega_e x_e$, etc. for the two electronic states.

Below is the Deslandres table for the $A^1\Pi - X^1\Sigma^+$ system of carbon monoxide (see heteronuc. diatomic MO diagram).

<table>
<thead>
<tr>
<th>$\nu'/\nu''$</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>64758 (2145)</td>
<td>62613 (2117)</td>
<td>60496 (2092)</td>
<td>58404 (2063)</td>
<td>56341 (2037)</td>
<td>54304 (2007)</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>(1476)</td>
<td>(1485)</td>
<td>(1487)</td>
<td>(1486)</td>
<td>(1487)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>66234 (2136)</td>
<td>64098 (2115)</td>
<td>59891 (2064)</td>
<td>57827 (2036)</td>
<td>55791 (2010)</td>
<td>53781 (1984)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(1448)</td>
<td>(1441)</td>
<td>(1444)</td>
<td>(1443)</td>
<td>(1443)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(1407)</td>
<td>(1413)</td>
<td>(1414)</td>
<td></td>
<td>(1410)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>69089 (2137)</td>
<td>66952 (2114)</td>
<td>64383 (64838)</td>
<td>60683 (2039)</td>
<td>58644 (1984)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(1378)</td>
<td>(1382)</td>
<td>(1370)</td>
<td>(1379)</td>
<td></td>
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<td></td>
</tr>
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<td></td>
<td>(1341)</td>
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<td>(1350)</td>
<td>(1343)</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>(1307)</td>
<td>(1305)</td>
<td>(1303)</td>
<td>(1299)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>73115 (2138)</td>
<td>70977 (2116)</td>
<td>68861 (2096)</td>
<td>66765 (2053)</td>
<td>64712 (2040)</td>
<td>62672 (1984)</td>
<td></td>
</tr>
</tbody>
</table>

Measurements are of the sharp edges of the band heads formed by fine rotational structure.

**Difference between wavenumbers in adjacent columns** correspond to vibrational level separations in the ground (lower) electronic state, and differences between **adjacent rows** to separations in the excited (upper) electronic state.

From this table, a series of averaged values of vibrational term values differences, $G(\nu+1)-G(\nu)$, can be obtained for both electronic states, and values of $\omega_e$, $\omega_e x_e$, etc. can be obtained from these. Note the large decrease in $\omega_e$ in the $A$ state results from promoting an e- from a bonding to an anti-bonding orbital, where the force constant is reduced!
Repulsive States & Continuous Spectra

(a) The ground configuration of the \( \text{He}_2 \) molecule is \((\sigma_g 1s)^2(\sigma_u^* 1s)^2\), and is expected to be unstable because of bonding/anti-bonding cancellation.

Thus, the \( X^1\Sigma_g^+ \) state has a potential energy curve with no minimum, and potential energy decreases smoothly as \( r \) increases. This is known as a repulsive state, since the atoms repel one another, and possesses no discrete vibrational energy levels (usually a continuum, though there may be a few if there is a very shallow minimum).

An electron can be promoted to give the configuration \((\sigma_g 1s)^2(\sigma_u^* 1s)^1(\sigma_g 2s)^1\), which has \( A^1\Sigma_u^+ \) and \( a^3\Sigma_u^+ \) bound states (the former is pictured above). The \( A-X \) transition is allowed, and gives rise to a continuum in emission between 60 and 100 nm.

(b) Discharge in molecular \( \text{H}_2 \) also gives a continuum in emission (160 - 500 nm). The transition is from the bound \( a^3\Sigma_g^+ \) to the repulsive \( b^3\Sigma_u^+ \) state, which arise from the \((\sigma_g 1s)^1(\sigma_g 2s)^1\) and \((\sigma_g 1s)(\sigma_u^* 1s)^1\) configurations. Dissociation gives two g.s. \( 1^2S_{1/2} \) \( \text{H} \) atoms.
Rotational Fine Structure

For electronic and vibronic transitions, the upper and lower electronic states are accompanied by stacks of rotational levels. These spectra can appear similar to rovibrational spectra, or markedly different, since transitions are not confined to $\Sigma-\Sigma$ types, upper and lower states may not have the same multiplicities, etc. The two most common types are the $^1\Sigma-^1\Sigma$ and $^1\Pi-^1\Sigma$ transitions.

The rotational term values are as usual:

$$F_v(J) = B_v J(J+1) - D_v J^2(J+1)^2$$

where $B_v$ is the rotational constant, $D_v$ the centrifugal distortion constant, and the $v$ subscripts indicate the vibrational dependence (of which only $B_v$ is important):

$$B_v = B_e - \alpha(v+1/2)$$

The constants $B_e$, $\alpha$ and $D_v$ are characteristic of a particular electronic state. The quantum number $J = 0, 1, 2, \ldots$ applied to the total angular momentum, excluding the nuclear spin (in $^1\Sigma$ states, only one type of angular momentum from rotation, and $\Lambda = 0$ and $S = 0$).

Labels $+, -, e$ and $f$ can be used in determining which transitions are allowed, though for $^1\Sigma-^1\Sigma$ electronic transitions, these labels can be ignored.

The rotational selection rule is $\Delta J = \pm1$, just as for a vibrational transition in a diatomic or linear polyatomic molecule, giving a $P$-branch ($\Delta J = -1$) and $R$-branch ($\Delta J = +1$). Each branch member is labelled as $P(J'')$ or $R(J'')$. 
Rotational Fine Structure, 2

Now, a more complete picture of the electronic spectrum arises, showing that it is possible to observe both vibrational coarse and rotational fine structure for high-resolution electronic spectra:

Each electronic state has a stack of vibrational levels which are more or less evenly spaced (except for anharmonicity), the spacing depends on the force constant for vibration.

Each vibrational state has a stack of rotational levels that spread out as rotation gets faster ($J$ gets bigger). The spacing between rotational levels can vary in different electronic states, since $B$ can change quite dramatically (i.e., $r_e$ quite different in different electronic states)
$^1\Sigma-^1\Sigma$ Electronic & Vibronic Transitions

Below are the rotational levels associated with two electronic $^1\Sigma^+$ states, transitions are allowed for + → - (and if homonuclear diatomic, $g \leftrightarrow u$). The sets are the same for two $\Sigma^-$ states, or if the upper state were $g$ and the lower $u$.

![Diagram showing rotational levels and transitions between different electronic states.](image)

An example of such a band is shown below for the $^1\Sigma-^1\Sigma$ transition of the short-lived RhN molecule:

There is notable asymmetry in this band, since the rotational constants $B'$ and $B''$ are typically very different in the different electronic states (dissimilar from the similar values of $B$ in different vibrational states).
$A^1\Sigma^+-X^1\Sigma^+$ transition in CuH

CuH is also a short-lived molecule, and has an even more asymmetric distribution of $P$ and $R$ branch peaks. There is convergence to form a band head, due to reversal of the $R$ branch, and corresponding divergence of the $P$ branch.

If the lower state is the ground electronic state, $r_e' > r_e''$, and therefore $B' < B''$, meaning that the rotational levels diverge more slowly in the upper than in the lower state.

In the case of CuH, $r_e$ increases from 1.463 Å in the $X^1\Sigma^+$ state to 1.572 Å in the $A^1\Sigma^+$ state.

If such rotational spectra are observed in emission, the rotational populations of the upper states determine the relative intensities of the transitions - these may or may not be determined by the Boltzmann distribution, depending on how the molecule wound up in the excited state.

Electronic spectroscopy provides a fifth method for heteronuclear diatomics for obtaining the internuclear distance in the ground state (others include rotational or vib-rot spectroscopy). However, this is the only method for looking at short-lived species (big advantage!!)
The rotational levels in the $^1\Pi$ state are different from those in the $^1\Sigma$ state because there are now two angular momenta: There is angular momentum $R$ due to end-over-end rotation of the molecule, and the component $\Lambda\hbar$ of orbital angular momentum along the internuclear axis ($\Lambda = 1$ for this state).

The resultant total angular momentum whose magnitude $B, J(J + 1)$, depends on the value of $J$, and since $J \geq \Lambda$, it cannot be less than one. So for the $\Pi$ state, $J = 1, 2, 3, \ldots$ and there is no $J = 0$ level, as shown on the next page.

Recall that all states with $\Lambda > 0$ are doubly degenerate, which can be thought of as arising (classically) from the clockwise and anti-clockwise motion of e- about the internuclear axis. The degeneracy may be split, due to interaction of the orbital motion and the overall rotation.

The splitting, $\Delta F(J)$, of the term values $F(J)$ due to this interaction is shown on the next page (exaggerated for clarity), and increases with the speed of the overall rotation (i.e., with increasing $J$):

$$\Delta F(J) = qJ(J + 1)$$

This is known as $\Lambda$-type doubling, and $q$ is constant for each electronic state.
The selection rule for the $^1\Pi - ^1\Sigma$ transition is $\Delta J = 0, \pm 1$, which gives $P$, $Q$ and $R$ branches. The figure below shows rotational fine structure where the $^1\Sigma$ state is the ground state, so $r_e' > r_e''$, and therefore $B' < B''$, and the $J$ levels converge much more rapidly in the $^1\Pi$ state. This means the $R$ branch converges, the $P$ branch diverges, and there is a small divergence in the $Q$ branch to smaller wavenumber.

The $g$ and $u$ subscripts and $s$ and $a$ labels apply only to a homonuclear molecule.
Selection Rules and AlH

The + and - (or e and f labels) are essential for the $^1\Pi - ^1\Sigma$ transition, telling us which of the split components in the $^1\Pi$ state is involved in the transition.

The + and - indicate whether the wavefunction is symmetric or antisymmetric w.r.t. reflection across any plane containing the internuclear axis. Whether the + is above or below the - component depends on the sign of $q$.

The selection rules: $+ \leftrightarrow -$, $+ \leftrightarrow +$, $- \leftrightarrow -$
result in $P$ and $R$ branches involving the upper components and the $Q$ branch involving the lower components.

The selection rules: $e \leftrightarrow f$ for $\Delta J = 0$ and $e \leftrightarrow e$, $f \leftrightarrow f$ for $\Delta J = \pm 1$ involving the alternative $e$ and $f$ labels suggest the same results.

The $A^1\Pi - X^1\Sigma^+$ electronic transition of AlH is above. The asymmetry in the spectrum is not due to a large change in $r_e$ ($r_e = 1.6478 \, \text{Å} \ & 1.648 \, \text{Å}$ in the $X^1\Sigma^+$ & $A^1\Pi$ states), but rather to the high value of $q = 0.008 \, \text{cm}^{-1}$ in the $A^1\Pi$ state.

Combination differences can be used to obtain $B''$ and $D''$, as well as $B_u'$ and $D_u'$ and $B_l'$ and $D_l'$ for the upper and lower components of the $^1\Pi$ state.
Emission and Lifetimes

Progressions with a common $v'$ state (below, $v' = 2$) can be observed only in emission spectra.

The observation could result from the random population of the $v' = 2$ levels, or observed under special conditions in which specially tuned monochromatic radiation which excites from $v'' = 0$ to $v' = 2$ with no collisions before emission (tunable laser used for this).

If emission occurs such that there is a transition between states with the same multiplicity, the result in **fluorescence**. If the emission is only from one vibrational level of the upper electronic state it is a **single vibronic level fluorescence**.

If emission occurs between states of different multiplicity, this is termed as **phosphorescence**.

A **radiative decay** process is one in which a molecule loses its excitation energy in the form of a photon.

A **non-radiative decay** process, which is more common, is one in which excess energy is transferred into motional modes (translation, vibration, rotation) of surrounding molecules via collision processes.

An excited molecule may also lose its excess energy by becoming involved in a **chemical reaction** (not discussed here, but covered in 59-241).
Fluorescence vs. Phosphorescence

In **fluorescence**, spontaneously emitted radiation stops immediately after the exciting radiation is terminated, whereas in **phosphorescence**, the spontaneous emission may persist for a long time period (from ms to hours).

**Fluorescence**: immediate conversion of absorbed radiation into re-emitted energy.
**Phosphorescence**: slow emission or “leaking” of stored energy from a reservoir.

A schematic representation of fluorescence is shown to the left. **Absorption** puts the molecule in an excited electronic state. The excited molecule has collisions with other molecules, and loses energy in a **non-radiative** (or **radiationless**) fashion, down to the lowest vibrational state. If the surrounding molecules are unable to accept enough energy to place the molecule back in the ground state, this state may last long enough to undergo **spontaneous emission**, and emit the remaining excess energy as radiation (fluorescence).
Fluorescence

The downward electronic transition is vertical, in accordance with the Franck-Condon principle, and has the vibrational characteristics of the lower electronic state.

The absorption spectrum arises from 0-0, 1-0, 2-0, etc. transitions which occur at progressively higher wavenumbers, with intensities governed by the FC principle.

The fluorescence spectrum arises from downward 0-0, 0-1, 0-2, etc. transitions, and peaks occur with decreasing wavenumbers - so the 0-0 absorption and fluorescence transitions are usually coincident.

It is possible for the 0-0 transitions to be different for samples in solution since the solvent molecules may interact differently with the solute in the ground and excited states.

Solvent molecules do not have time to rearrange during the transition, environments different for each process: for absorption spectra, the solvated ground state is observed, whereas for fluorescence, the solvated excited state is observed.
Fluorescent Dyes & Quenching

Fluorescence occurs at the lower frequency than incident radiation, since emission happens after non-radiative loss of energy into the surroundings. Fluorescence is often described as “emission of a red-shifted photon right back into the ground state”.

This explains the behaviour of fluorescent dyes, which have vivid orange, red and green colours. These dyes absorb in the UV and blue regions of the visible spectrum, and fluoresce in the visible region, giving rise to extremely vivid colours.

Some solvent molecules can influence the intensity of fluorescence - this depends on their ability to accept vibrational and electronic quanta during the non-radiative decays. For instance, H₂O, which has widely spaced vibrational levels, and can easily accept large quanta of electronic energy, thereby eliminating or quenching fluorescence.
Phosphorescence

Phosphorescence resembles fluorescence in the absorption portion of the process, but the presence of a triplet state and selection rules differentiate the two processes.

The singlet and triplet states have a common geometry (same $r_e$) where potential energy curves intersect. Thus, if the electron spins can unpair (i.e., conversion of $\uparrow \downarrow$ to $\uparrow \uparrow$), the molecule may undergo intersystem crossing (ISC) and become a triplet state.

Singlet-triplet transitions may occur only in the presence of spin-orbit coupling (atoms & molecules), which happens when molecules have heavier atoms (e.g., S, P, etc.)

As the molecule enters the triplet state, it continues non-radiative decay down the vibrational ladder to the lowest vibrational energy level (which is lower than the singlet state). If (1) the solvent cannot absorb the final large quantum of electronic energy (i.e., poor quenching), and (2) molecule cannot radiate its energy because returning to the ground state is spin-forbidden, then phosphorescence can occur. The radiative transition is not totally forbidden, since the spin-orbit coupling that caused the ISC also breaks the selection rule!
Phosphorescence, 2

“Phosphoring” or phosphorescent molecules weakly emit radiation, and this emission can continue long after the application of the exciting radiation.

Energy appears to be trapped in a slowly leaking reservoir, and is very intense from solid materials (since energy transfer from collisions is much less efficient than other phases, and ISC has plenty of time to occur).

Phosphorescence also requires the presence of a heavy atom, and hence the corresponding large spin-orbit coupling.

used in “nightglow” watches.

Cathode Ray tubes (computer monitor, TV, oscilloscope, etc.)

phosphorescent materials:

La$_2$O$_2$S:Tb (P44-green) InBO$_3$:Eu + InBO$_3$:Tb + ZnS:Ag (white)
**Dissociation & Predissociation**

An electronically excited molecule may also lose energy through **dissociative processes** (i.e., bond breaking).

The onset of dissociation can easily be spotted in electronic spectra with vibrational fine structure, where the band will terminate at a specific energy. Absorption happens in the continuous band of energy levels above this **dissociation limit**, since the final state is unquantized translation of the “pieces” or atoms of the molecule.

If vibrational structure disappears but resumes at higher photon energies, this can be interpreted as **predissociation**. When a molecule is excited to a vibrational level, e- may undergo a reorganization that results in an **internal conversion** (IC), which is a radiationless conversion to another state of the same multiplicity.

The IC occurs readily at the **intersection** of the p.e. curves, where nuclear geometries of the two states are the same. The molecule may convert into a dissociative state, so states near the intersection have a finite lifetime & energies are imprecisely defined: thus the fine structure is **blurred** in the vicinity of the intersection. If molecule is excited above this level, normal vibrational structure is observed.
Jablonski Diagram

There are a variety of styles for the Jablonski diagrams, that show all of the absorption and emission processes, including fluorescence, phosphorescence, ICS, IC, dissociation, non-radiative decay, etc:

A Jablonski diagram, which shows the ground singlet state $S_0$, two excited singlet states $S_1$ and $S_2$, and a triplet state, $T$. Various possible processes are represented. The internal conversions $S_2 \rightarrow S_1$ and $S_1 \rightarrow S_0$ are often at the same energy because the excited states often lie within the potential energy surface of the lower energy state.

Some other p.e. curves for dissociation, predissociation and phosphorescence are below:
Key Concepts

1. MO’s in diatomics give rise to bonding (bound), anti-bonding (repulsive) and non-bonding (dissociative) potential energy curves.

2. Each electronic state has a set of vibrational levels. Under certain circumstances, usually gas phase and/or high-resolution experiments, it is possible to observe vibrational coarse structure in electronic spectra.

3. Vibrational transitions which accompany the electronic transitions are called vibronic transitions. These transitions give rise to bands in the spectrum, and a set of bands associated with a single electronic transition is the electronic band system. Progressions involve sets of vibronic transitions with a common upper or lower level, and groups of vibronic transitions with the same $\Delta \nu$ are sequences.

4. The Franck-Condon principle classically and quantum mechanically explains the intensities of peaks arising from vibronic transitions.

5. Rotational fine structure can also be observed in electronic spectra, giving rise to interesting patterns of $P$, $Q$ and $R$ branches. The $^1\Sigma-^1\Sigma$ and $^1\Pi-^1\Sigma$ transitions in diatomics are discussed.

6. Consideration is given to the fate of excited states and associated energies: fluorescence, phosphorescence, intersystem crossing, internal conversions, non-radiative transitions, etc. are considered in detail. All are summarized in a Jablonski diagram.