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WINTER COLLEGE ON

ATOMIC AND MOLECULAR PHYSICS

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MOLECULAR SPECTRA III

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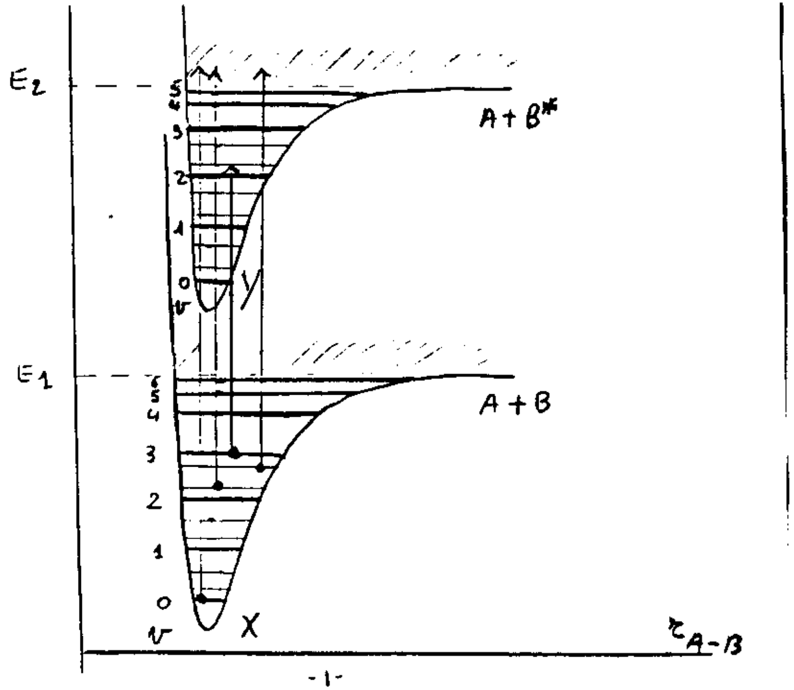
Lecture 4

iii) Diffuse and continuous electronic spectra

Continuous electronic spectra.

Continuous spectra of molecules are observed in absorption and in emission and are due to dissociation processes (rupture of a chemical bond). To clarify the mechanism of continuous spectra formation, reference is made to the following figure, where are reported the potential energy curves of 2 different electronic states of a diatomic molecule AB.

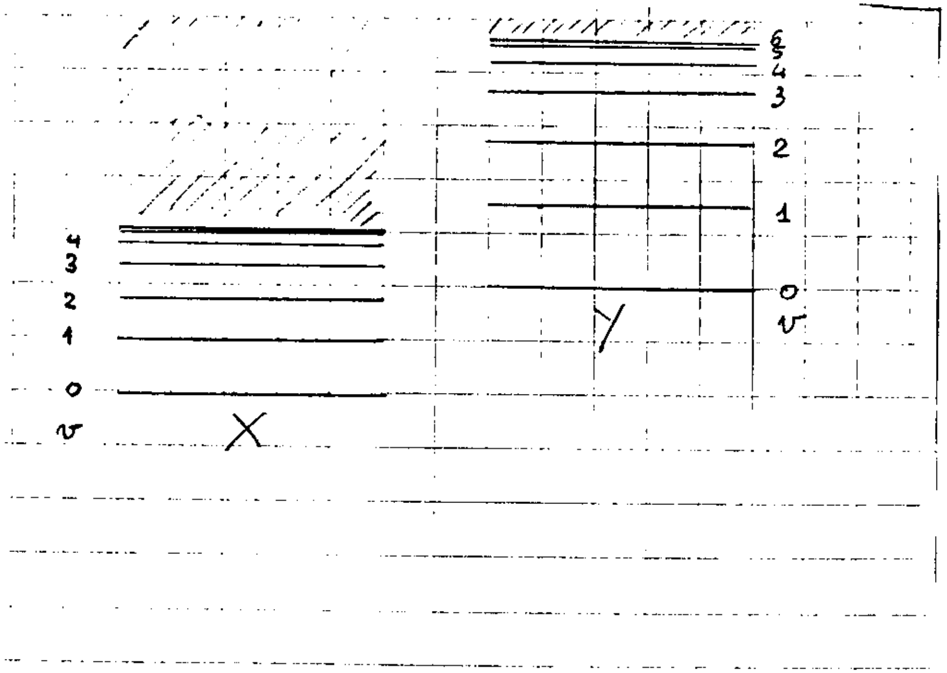
An electronic transition between states X and Y is in fact made up by several rovibronic (rotational-vibrational-electronic) transitions. Some of these are indicated by arrows in the fig. E_1 and E_2 are the dissociation energies of states X and Y. Absorptions which end up above E_2 correspond to the rupture of the bond of AB and originate a continuous absorption. The general appearence of the absorption spectrum will be that of a band system converging toward a continuum.



Other cases where continua are observed, involve transitions between states without minimum in the potential energy curve.

Diffuse electronic spectra.

Line broadening, not due to the mechanisms discussed in lecture 5, are usually due to radiationless transitions between a discrete state and a continuous state of the same or nearly the same energy. The following figure represents 2 sets of vibronic levels of a diatomic molecule, where there is overlapping of the discrete levels of state Y with the continuous levels of state X



Diffuse spectra are particularly frequent in polyatomic molecules, where, at a variance of diatomics, several dissociation limits are possible.

As for continuous spectra, information provided from diffuse spectra is concerned with dissociation energy and thus bond energies in molecules.

Intensity, lifetimes and line broadening

i) Selection rules, transition moments for rotational, vibrational and electronic transitions.

Rotational transitions of diatomic or linear polyatomic molecules.

The eigenfunctions of the rigid rotor are

$$\Psi_{JM} = N_{JM} P_J^{|M|} (\cos\vartheta)\, e^{iM\varphi} ,$$

commonly known as surface spherical harmonics. The transitions occurring are those between states for which the transition dipole moment matrix elements are different from zero:

$$\mathbb{R}^{J'M';\, J''M''} = \int \psi_{J'M'}\, \underline{\mu}\, \psi_{J''M''}\, d\tau \neq 0$$

The selection rules arising from the above conditions are:

1) the molecule must have a non-zero permanent electric dipole moment

2) $\Delta J = J' - J'' = \pm 1$

3) $\Delta M = M' - M'' = 0 ; \pm 1$

Since the rotational energy is independent of M, if no electric external field is present, the selection rule 3) need be not considered.

Vibrational transitions in diatomic molecules.

The harmonic oscillator eigenfunctions, are

$$\psi_v = N_v\, e^{-\frac{1}{2}\alpha x^2} H_v(\sqrt{\alpha}\, x)$$

N_v = normalizing constant

$\alpha = 4\pi^2 \mu \nu / h$

$H_v(\sqrt{\alpha}\, x)$ = Hermite polynomial of degree v.

= reduced mass

As for rotation, it is necessary that the molecule has a permanent electric dipole moment, moreover, the matrix elements of the dipole moment operator

$$\mathbb{R}^{v';v''} = \int \psi_{v'}\, \underline{\mu}\, \psi_{v''}\, dx$$

are non-zero, only il $v' - v'' = \Delta v = \pm 1$.

As for rotation, only adiacent states are connected by the electric dipole radiation.

Electronic transitions in diatomic molecules.

As we have previously pointed out, there is not a simple model for the electronic motion in diatomic molecules: as a consequence, it is not possible to derive the selection rules directly from the matrix elements of the transition dipole moment.

Rather, the symmetry properties of the combining wavefunctions are exploited to derive the selection rules.

The quantum numbers Λ , S and Σ (in states with $\Lambda \neq 0$), and the two symmetry properties of ψ_e in homonuclear and one in heteronuclear diatomics will be employed to express the electric dipole selection rules.

Selection rules:

1) $\Delta\Lambda = 0 ; \pm 1$

2) $\Delta S = 0$ (only for molecules without heavy nuclei)

3) $\Delta\Sigma = 0$ and $\Delta\Omega = 0 ; \pm 1$ for transitions between multiplets components.

4) $+ \longleftrightarrow +$; $- \longleftrightarrow -$; but not $+ \longleftrightarrow -$
$g \longleftrightarrow u$ but not $g \longleftrightarrow g$ or $u \longleftrightarrow u$