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WINTER COLLEGE ON
ATOMIC AND MOLECULAR PHYSICS

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MOLECULAR SPECTRA I

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Lecture 2

Molecular Spectra

i) Diatomic Molecules

Separation of electronic and nuclear motions.

The hamiltonian operator of a molecule (apart the kinetic energy of the molecule as a whole) is given by:

$$[1] \qquad \underline{H} = -\sum_{\alpha} \frac{\hbar^2}{8\pi^2 M_\alpha} \nabla_\alpha^2 - \sum_i \frac{\hbar^2}{8\pi^2 m} \nabla_i^2 + V_{en} + V_{ee} + V'_{nn}$$

The first two terms represent the kinetic energy of the nuclei and of the electrons, while the remainder are potential energy terms, arising from coulombic attraction (V_{en}) and repulsions (V_{ee} and V_{nn}) between electrons (e) and nuclei (n).

For fixed nuclei (no nuclear kinetic energy and V_{nn} constant), we look for a solution Ψ_e of the equation

$$[2] \qquad \underline{H}_e \Psi_e = E_e \Psi_e \; ,$$

with $\underline{H}_e = -\sum_i \frac{h^2}{8\pi^2 m} \nabla_i^2 + V_{ne} + V_{ee}$ and $\Psi_e = \Psi_e(r_e, r_n)$, that is Ψ_e (and E_e) depends on nuclear coordinats r_n. In the Born-Oppenheimer approximation, the nuclei are assumed to move slowly relatively to the electrons: as a consequence in Ψ_e and E_e the nuclear coordinates r_n enter as parameters.

We write the wave equation for the complete system, assuming $\Psi = \Psi_e \times \Psi_n$, with $\Psi_n = \Psi_n(r_n)$,

$$[3] \qquad \underline{H}\, \Psi_e \Psi_n = E\, \Psi_e \Psi_n$$

Using eq.[2] and neglecting terms where appear first and 2nd derivatives of Ψ_e respect the nuclear coordinates, we obtain:

$$[4] \qquad (\underline{H}_n + E_e)\Psi_n = E\Psi_n$$

with $\underline{H}_n = -\sum_\alpha \frac{h^2}{8\pi^2 M_\alpha} \nabla_\alpha^2 + V_{nn}$.

Within the limits of the present approximation, the electronic energy E_e can be considered as a part of the potential energy of the nuclei.

The electronic states.

The solution of eq.[2] is possible only for very simple molecules, where the number of electrons is not larger than about 20.

We will discuss briefly the classification of the electronic states.

All electron orbital angular momenta and all electron spin angular momenta are coupled to give the resultant L and S respectively.

The spin-orbit coupling between S and L is weak and only the components Λ of L along the internuclear axis is a good quantum numbers.

Electronic states are disegned: Σ ; Π ; Δ ; Φ ... corresponding to $\Lambda = 0 ; 1 ; 2 ; 3 ; \ldots$ Also S is coupled to the internuclear axis, and the projection of S can take the values:

$$\Sigma = S \; ; \; S-1 \; ; \ldots \; -S$$

There are $2S+1$ components for a given state with $\Lambda > 0$, which are identified according to the quantum number $\Omega = |\Lambda + \Sigma|$, attached as a subscript to the term symbol, while the multiplicity of the state $(2S+1)$ is indicated as a superscript.

Example: a $^3\Pi$ state ha $\Lambda = 1$ and $S = 1$; the possible values of Ω are 2 ; 1 ; 0 and the corresponding states are:

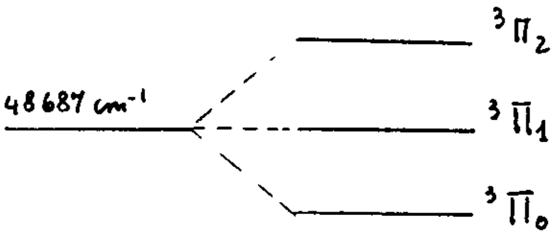
$$^4\Pi_2 \; ; \; ^4\Pi_1 \; ; \; ^4\Pi_0$$

Spin-orbit interaction splits the multiplet components according to the equation:

$$E = A\,\Lambda\,\Sigma$$

where A is the spin-orbit coupling constant.

For the $^3\Pi$ state of CO 48687 cm^{-1} above the ground state, $A = 41.5$ cm^{-1}:



In addition to the quantum numbers Λ, S, Σ and Ω, the electronic states of diatomic molecules are labelled by symmetry properties of the wavefunctions.

For $\Lambda = 0$ states (Σ states) the reflection in a plane passing through the atoms leaves the wavefunction unchanged Σ^+ or with sign changed Σ^-.

For equal charge nuclei diatomic molecules the electrons move in a centrosymmetric field and again the electronic wavefunction is unchanged (g) or change sing (u) following a reflection at the center.

The symmetry property g and u is added as a subscript to the term symbol: the lowest electronic state of molecular oxygen is a $^3\Sigma_g^-$.

The rotational and vibrational energies and the quantum-mechanical models.

The rigid rotor as a model for rotational motion of a diatomic molecule. The Hamiltonian operator in spherical coordinates of the rigid rotor is:

$$\underline{H}^R = -\frac{h^2}{8\pi^2 I}\left[\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial}{\partial\vartheta}\right) + \frac{1}{\sin^2\vartheta}\cdot\frac{\partial^2}{\partial\varphi^2}\right]$$

I = moment of inertia in the principal inertial axis system.

The solution of the 2nd order differential equation:

$$\underline{H}^R \psi_r = E^r \psi_r$$

gives the eigenfunctions $\psi_r = N_{J,M} P_J^{|M|}(\cos\vartheta)\, e^{iM}$

$N_{J,M}$ being the normalizing factor, and $P_J^{|M|}(\cos\vartheta)$ the associate Legendre polynomials, and

$$E_J^r = \frac{h^2}{8\pi^2 I} J(J+1) = BJ(J+1) \qquad J = 0;\ 1;\ 2; \dots$$

B is called rotational constant.

The simple harmonic oscillator as a model for vibrational motion of a diatomic molecule.

The Hamiltonian operator in this case is:

$$\underline{H} = -\frac{h^2}{8\pi^2\mu}\frac{d^2}{dx^2} + \frac{K}{2}x^2$$

K = force constant

The wavefunctions

$$\psi_v(\xi) = N_v H_v(\xi)\, e^{-\xi^2/2}$$

$\xi = \sqrt{\alpha}\, x$

$\alpha = \frac{2\pi\sqrt{\mu K}}{h}$

μ = reduced mass

v = vibrational quantum number

$$E_v = (v + \tfrac{1}{2})\, h\nu \qquad v = 0;\ 1;\ 2;\ \dots$$

$$\nu = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}}$$

Spectra of a diatomic molecule in different region of the electromagnetic spectrum.

Microwave and far-infrared regions.

The following table reports the frequencies of rotational transitions of CO. The first seven measurements were obtained with mmwave sources, while the 5 data at higher frequencies were measured with a tunable far-infrared radiation generated by CO_2 laser difference in metal-insulator-metal diode. The spectrum consists of a branch of line equally spaced in first approximation, as required by the selection rule $\Delta J = 1$, applied to the equation

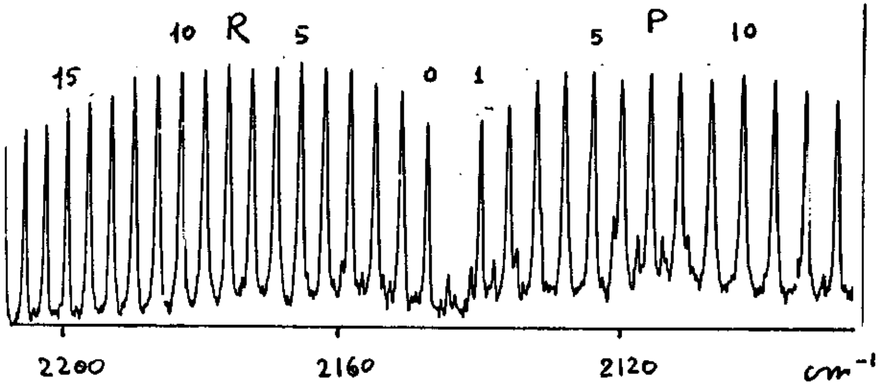
$$E^{r}_{J} = B\,J\,(J+1).$$

The transitions from level J to level J + 1, appear at frequency:

$$\nu_J = 2B\,(J+1)$$

Infrared region.

In the next figure is presented the ro-vibrational fundamental transition of CO centered at 2144 cm^{-1}



CO ROTATIONAL TRANSITIONS

Calculated Frequency in:

J'-J"	cm^{-1}	MHz	OBS-CALC (MHz)
1- 0	3.845 033 3	115 271.20	0.00
2- 1	7.689 919 7	230 538.00	-0.03
3- 2	11.534 512	345 795.98	0.01
4- 3	15.378 664	461 040.75	0.06
5- 4	19.222 228	576 267.91	0.01
6- 5	23.065 058	691 473.05	-0.07
7- 6	26.907 006	806 651.77	0.01
8- 7	30.747 927	921 799.67	
9- 8	34.587 673	1 036 912.35	
10- 9	38.426 097	1 151 985.40	
11-10	42.263 052	1 267 014.44	
12-11	46.098 393	1 381 995.05	
13-12	49.931 972	1 496 922.86	
14-13	53.763 642	1 611 793.45	
15-14	57.593 258	1 726 602.45	0.02
16-15	61.420 673	1 841 345.45	
17-16	65.245 740	1 956 018.07	
18-17	69.068 313	2 070 615.93	
19-18	72.888 246	2 185 134.63	
20-19	76.705 392	2 299 569.80	-0.11
21-20	80.519 606	2 413 917.05	
22-21	84.330 741	2 528 172.00	
23-22	88.138 651	2 642 330.29	
24-23	91.943 191	2 756 387.53	0.05
25-24	95.744 215	2 870 339.37	
26-25	99.541 578	2 984 181.42	
27-26	103.335 132	3 097 909.33	0.03
28-27	107.124 734	3 211 518.74	
29-28	110.910 238	3 325 005.30	
30-29	114.691 499	3 438 364.63	
31-30	118.468 371	3 551 592.41	
32-31	122.240 710	3 664 684.28	
33-32	126.008 370	3 777 635.90	
34-33	129.771 207	3 891 442.92	-0.02
35-34	133.529 077	4 003 101.02	

The formation of 2 branches in this type of transition, instead of a single one as in rotational spectra is easy understood in terms of selection rules for rotational energy:

R - branch	$\Delta J = +1$	as in rotation
P - branch	$\Delta J = -1$	not possible in rotation.

In addition, the harmonic oscillator selection rule $\Delta v = 1$ is in action.

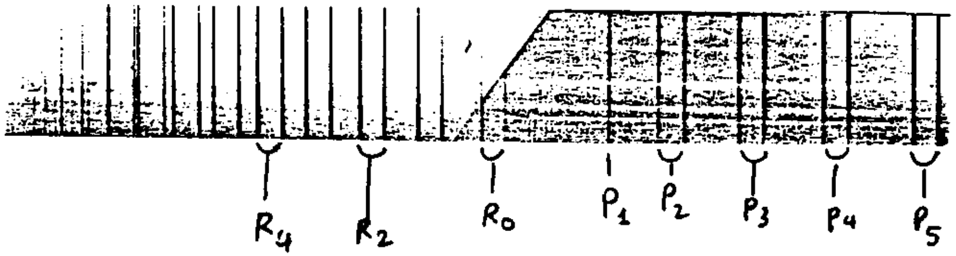
Visible and u.v. regions.

In this spectral region fall the electronic transitions.

Two example are presented in the following figures:

1) The visible absorption band of O_2 (oxygen) at about 13 200 cm^{-1} (~ 758 nm) very weak, being forbidden by selection rules (see lecture 4)

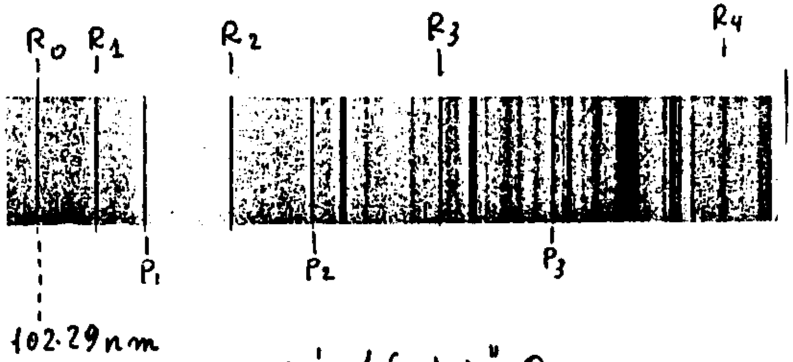
$$^1\Sigma_g^+ \leftarrow {}^3\Sigma_g^-$$



vibrational numbering
$v' = 1$; $v'' = 0$

2) The vacum u.v. absorption of HF (hydrogen fluoride) at 98000 cm^{-1} (~102 nm)

$^1\Sigma^+ - {}^1\Sigma^+$ band of HF



$v' = 16$; $v'' = 0$

The 2-branch structure of the ro-vibrational spectra is still present, but they are less easily recognized, because the rotational B constants of the combining states are now sensibly different. As a consequence, one of the branch may present a turning point.

Structure of the molecules from their spectra.

The analysis of the spectra of diatomic molecules provides a series of information on structure, which are summarized below:

a) Energy levels and ionization energy

b) The rotational constant B gives the interatomic distance

c) From the vibrational spacing one cam obtain the potential energy curve, and the dissociation (bond) energy

d) Electronic configuration