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WINTER COLLEGE ON
ATOMIC AND MOLECULAR PHYSICS

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MOLECULAR SPECTRA II

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Lecture 3

ii) Polyatomic molecules

Understanding the spectra of polyatomic molecules starting from diatomics.

Rotations of non-linear polyatomic molecules.

In a non-linear polyatomic molecule there are 3 moments of inertia, in the principal axis system, different from zero. Following the convention:

$$I_c \geqslant I_b \geqslant I_a$$

where a , b , and c identify the principal axis, we classify the molecules, from the point of view of rotation, as follow.

$I_c = I_b > I_a$	prolate symmetric rotor
$I_c > I_b = I_a$	oblate symmetric rotor
$I_c > I_b > I_a$	asymmetric rotor
$I_c = I_b = I_a$	spherical rotor

The energy in the first 2 cases is given respectively by:

$$E_p = B J (J+1) + (A-B) K^2$$

$$E_o = B J (J+1) + (C-B) K^2$$

The meaning of the symbols is the following:

$$A = \frac{h}{8\pi^2 I_a} \quad ; \quad B = \frac{h}{8\pi^2 I_b} \quad ; \quad C = \frac{h}{8\pi^2 I_c}$$

$J = 0;\ 1;\ \ldots\ldots$; the same as in diatomic molecules

$K = 0;\ 1;\ 2;\ \ldots\ J$; is the component of J along the a-axis (prolate) or the c-axis (oblate) which usually is a symmetry axis of the molecule.

For asymmetric rotors there is not a formula in closed terms for the rotational energy. This is derived by computing techniques, involving the diagonalization of tridiagonal matrices of approximate dimensions J/2. Only J is a well defined quantum number for asymmetric rotors.

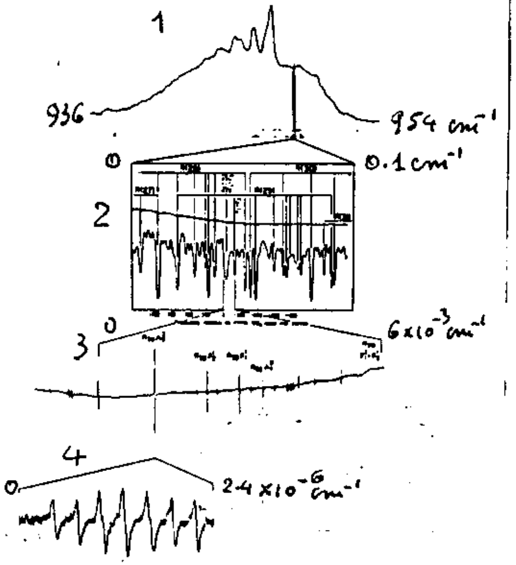
The spherical rotor rotational energy is:

$$E_s = B J (J+1)$$

Polyatomic molecules, having larger principal moments of inertia and thus smaller rotational constants than diatomics; will have molecular spectra less easily resolved in individual lines.

The density of lines is further increased by the larger number of states with the same J and different K .

In the following figure is shown a small portion of the vibrational spectrum of SF_6 (sulfur exafluoride), taken at various resolutions.



1) low-resolution 0.07 cm⁻¹ - Only the envelope of various branches

2) Doppler-limited spectrum. Some fine rotational structure is resolved

3) Sub-doppler spectrum: the rotational structure is resolved

4) Hyperfine structure of single rotational lines.

Vibrations in polyatomic molecules.

A N-atomic molecule has 3N-6 normal modes of vibration (3N-5 if linear), in each of which all the nuclei perform harmonic oscillations around their equilibrium positions, in phase and with the same frequency.

To a first approximation, each normal mode correspond an harmonic oscillator with frequency of the normal mode, and given by the same equation reported for a diatomic molecule.

In this way, a N-atomic molecule, is a collection of 3N-6 harmonic oscillators, with total vibrational energy:

$$E = \sum_{i=1}^{3N-6} \nu_i \, (v_i + \tfrac{1}{2}) \qquad v_i = 0;\ 1;\ 2;\ 3;\ \ldots.$$

v_i = vibrational quantum number of i-th normal mode

ν_i = vibrational frequency of the i-th mode.

As for the rotational states, the density of vibrational states may become very high.

The following equation gives the density (number of vibrational levels per cm^{-1}) of stats:

$$D = \frac{E^{3N-7}}{(3N-7)!\,\prod_i \nu_i}$$

N = number of atoms in the molecule

E = vibrational energy

ν_i = frequency of normal vibrations.

For a 4-atom molecule, like CH_2O (formaldeide), with $\nu_1 = 2766$; $\nu_2 = 1746$; $\nu_3 = 1501$; $\nu_4 = 1167$; $\nu_5 = 2843$; $\nu_6 = 1251$; alla data are in cm^{-1} units,

at $E = 15{,}000\ cm^{-1}$, the density is 0.2 state/cm^{-1}; every 5 cm^{-1}, there is a vibrational state.

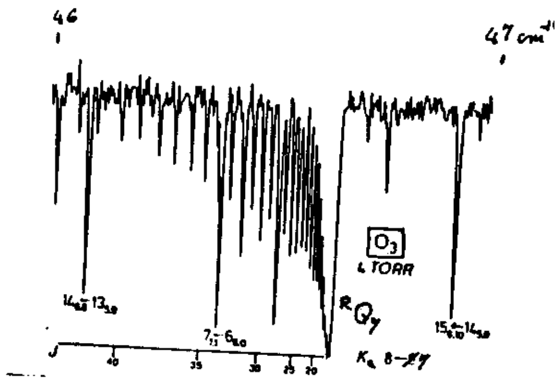
It should be clear that the spectral analysis, that is the identification of states connected by a transition, is much more complicated for polyatomic than for diatomics molecules. This is a consequence of the more complicated structure of ro-vibrational levels. A further factor, which reduces the possibility of spectral analysis in polyatomics, is the line broadening due predissociation (see lecture 4) much more frequent than in diatomics.

The information on molecular structure from spectral analysis, is the same discussed in lecture 2 on diatomics molecules.

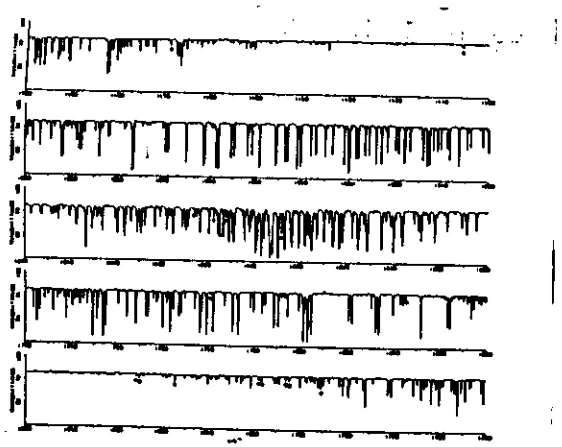
The most important limitation, in respect to diatomics, concerns the information on geometrical structure.

A maximum of 3 moments of inertia, can be obtained from the rotational analysis; and this allows the determination of 3 geometrical parameters (bondlengths and angles). Isotopically substituted molecules can add to the information, but this may be not enough for large molecules with little or not symmetry.

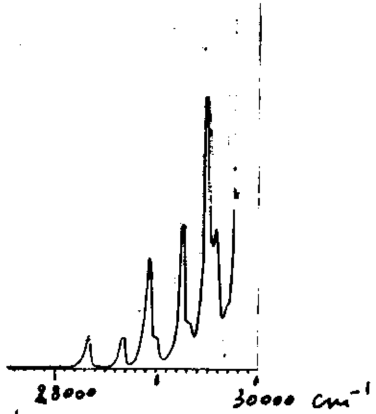
In the following figures are presented some spectra of polyatomic molecules, in different spectral region with the indication of the information which can be obtained from them.



A short portion of the rotational spectrum of ozone O3 - Moments of inertia of the ground state; rotational energy levels, are the data which can be extracted from this spectrum



Rotational structure of the ν_4 and $2\nu_2$ bands of ammonia $^{15}NH_3$, between 1400 and 1850 cm^{-1}. Analysis of this spectrum provides the rotational energy levels of the ground, $v_4=1$ and $v_2=2$ states.



Vibrational structure of the near u.v. electronic transition in absorption of ozone (O_3). No rotational structure is observed because of the diffuseness. Vibrational energy levels of the upper electronic state are obtained from the analysis.