

Pure Rotational Spectra of Asymmetric Molecules

For asymmetric top molecules (most of the system)

$$I_c > I_B > I_A \quad \text{and} \quad A > B > C.$$

Asymmetric molecules have complex energy patterns.

It is found to be easier to study such molecules by comparing them with symmetric ones (prolate and oblate tops).

We call them "near-symmetric top" systems.

For $I_c \approx I_B > I_A$ "Near-prolate top".

For $I_c > I_B \approx I_A$ "Near-oblate top".

Degree of asymmetry is given by the "asymmetric parameter" κ .

κ is called Ray's asymmetry parameter

$$\kappa = \frac{2B - A - C}{A - C} \quad ; \quad -1 \leq \kappa \leq +1$$

$\kappa = -1$ Prolate symmetry
 $\kappa = 0$ Most asymmetric
 $\kappa = +1$ Oblate symmetry

} κ measures the degree to which a molecule deviates from being a symmetric rotor.

The classical energy expression is:

$$E_r = \frac{P_a^2}{2I_A} + \frac{P_b^2}{2I_B} + \frac{P_c^2}{2I_C} \quad ; \quad I_A \neq I_B \neq I_C$$

Quantum mechanically, the Hamiltonian operator is:

$$\hat{H} = \frac{\hat{P}_a^2}{2I_A} + \frac{\hat{P}_b^2}{2I_B} + \frac{\hat{P}_c^2}{2I_C} \quad ; \quad I_A \neq I_B \neq I_C$$

where $A = \frac{\hbar^2}{2I_A}$, $B = \frac{\hbar^2}{2I_B}$ and $C = \frac{\hbar^2}{2I_C}$

A, B, and C are in joules.

Energy of rotational levels for asymmetric rotor is given by:

$$F(J, \tau) = \frac{1}{2} (A+C) J(J+1) + \frac{1}{2} (A-C) E_{J\tau}(K)$$

τ : a label "not a Q.N." used to distinguish the degenerate $2J+1$ levels of a specific value of J .

$$\tau = J, J-1, \dots, 0, \dots, -J+1, -J$$

Here τ is related to the quantum numbers K_a and K_c by

$$\tau = K_a - K_c$$

$\begin{array}{ccc} & \uparrow & \leftarrow \\ & \text{prolate} & \text{oblate} \end{array}$

$E_{J\tau}(K)$: a function of the asymmetry parameter K

→ How rotational levels are labeled in case of asymmetric top molecules?

It is labeled by $\bar{J}_{K_a K_c}$ or \bar{J}_{τ}

Example: $J=3$, $K_{\text{prolate}}=2$, $K_{\text{oblate}}=1$

3_{21} level or 3_1

In the case of asymmetric rotors, each rotational level with a specific J value is split into $2J+1$ levels.

The magnitude of splitting is proportional to the degree of asymmetry of the molecule (How close is K to zero).

A correlation diagram that connects the prolate top with oblate top symmetric molecule rotational levels is useful to understand the numbering system for asymmetric top molecules.

Example: Draw the energy levels of a near-prolate top molecule with the below information:

$A = 0.20 \quad B = 0.11 \quad C = 0.10$

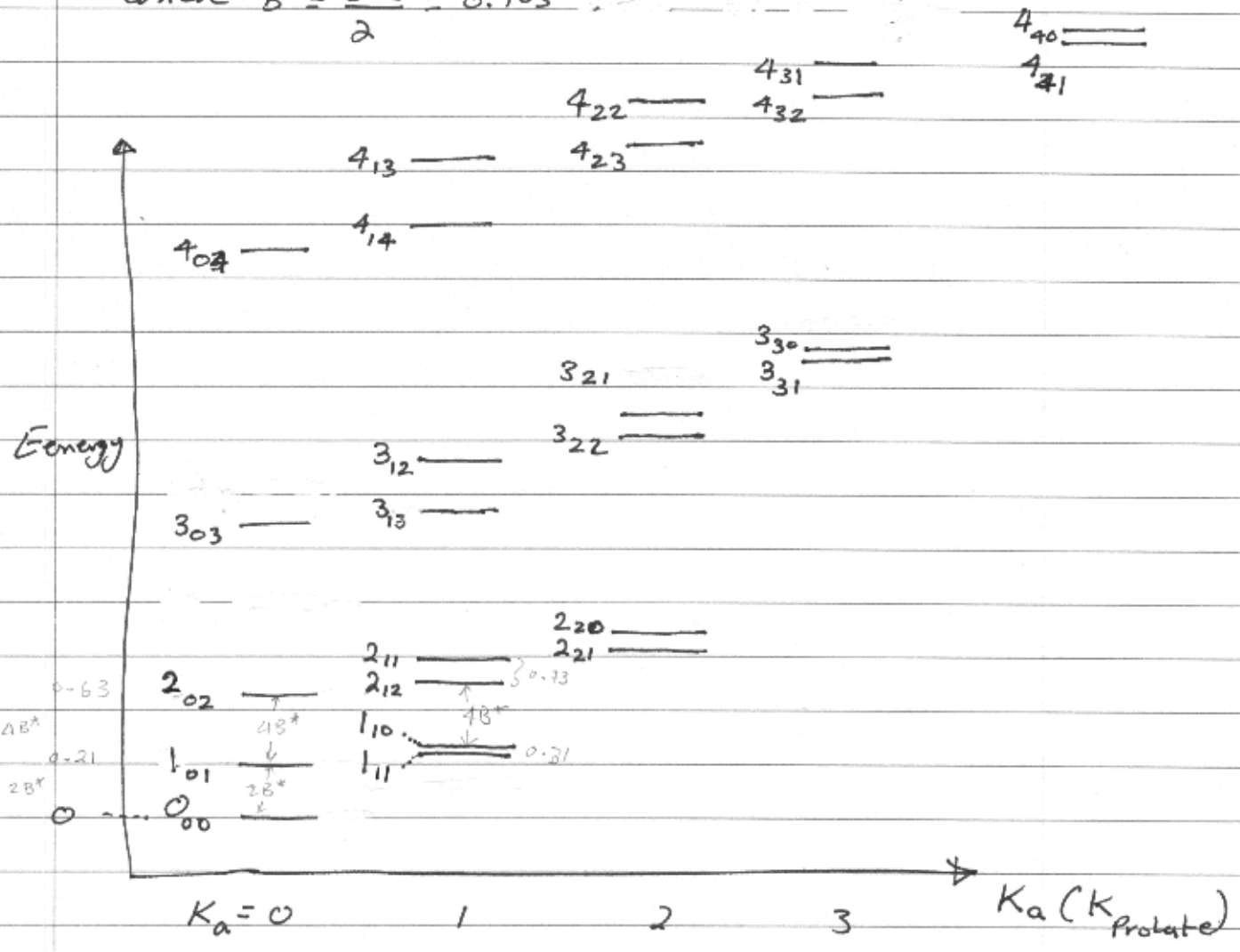
$$K = \frac{2B - A - C}{A - C} = \frac{0.22 - 0.20 - 0.10}{0.20 - 0.10} = -0.8$$

Approximate energy levels:

$$F(J, K) = B^* J(J+1) + (A - B^*) K_a^2$$

Near-prolate

where $B^* = \frac{B+C}{2} = 0.105$



Selection Rules for asymmetric rotors

⊗ $\Delta J = 0, \pm 1$

$\Delta J = 0$ is called Q-branch transitions.

$\Delta J = +1$ is called R-branch

$\Delta J = -1$ is called P-branch

In reality, $\Delta J = 0$ is applied for linear and symmetric molecules. Yet, such transitions in these types of molecules would result in zero-frequency transitions.

The splitting in the K degeneracy in asymmetric molecules causes the Q-branch transitions in asymmetric molecules, and not symmetric and linear molecules, to be observed.

⊗ The selection rule governing the K levels is more complicated. It can be summarized as:

Type of transition

selection Rule

A-type

$\Delta K_a = 0$

$\Delta K_c = \pm 1$

B-type

$\Delta K_a = \Delta K_c = \pm 1$

C-type

$\Delta K_a = \pm 1$

$\Delta K_c = 0$

A-type transition

It is observed when the dipole moment component along the a-axis (μ_a) is not zero.

$$\mu_a \neq 0$$

Same thing is said for:

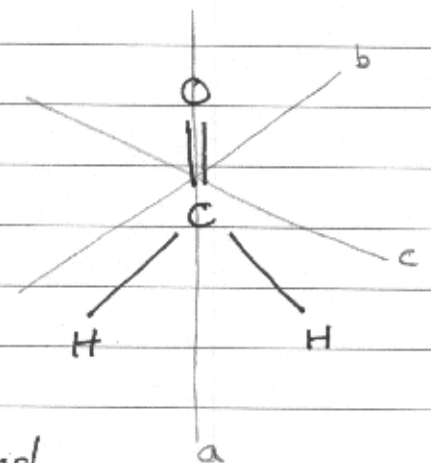
B-type transition when $\mu_b \neq 0$.

C-type transition when $\mu_c \neq 0$.

For example, formaldehyde experiences only A-type transitions because:

$$\mu_a \neq 0$$

$$\mu_b = \mu_c = 0$$



Thus only a-type transitions, and not b-type and c-type transitions, are observed.

It would then follow the selection rules:

$$\Delta J = 0, \pm 1$$

$$\Delta K_a = 0$$

$$\Delta K_c = \pm 1$$

Spherical Top Molecules

In spherical rotors :

$$I_A = I_B = I_C \quad \text{and} \quad A = B = C$$

According to the ^{non-}polarity of spherical rotors, ^(no dipole moment) there should be no transitions in their rotational spectra.

However, centrifugal distortion in such rotors may produce a small dipole moment which would enable in observing pure rotational spectra.

For example, due to internal rotation, centrifugal distortion results in very small dipole moments in CH_4 and SiH_4 of the order of $10^5 - 10^6 \text{ D}$.

Selection Rule

$$\Delta J = \pm 1$$

An approximate spacing of $2B$ is observed.