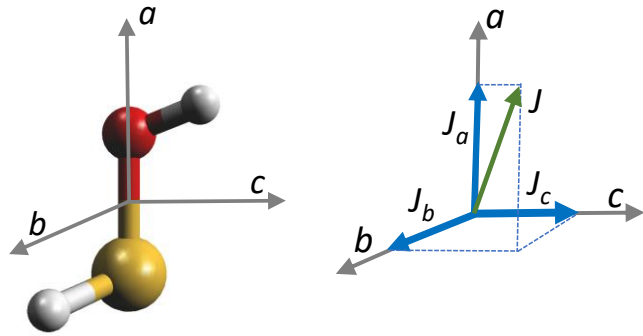


Introduction to PGopher - The ABC of Spectroscopy

- 1) The rotation of a molecule is described in the principal axes system (PAS)
The axes are labeled a, b, c , according to the moments of inertia: $I_a < I_b < I_c$



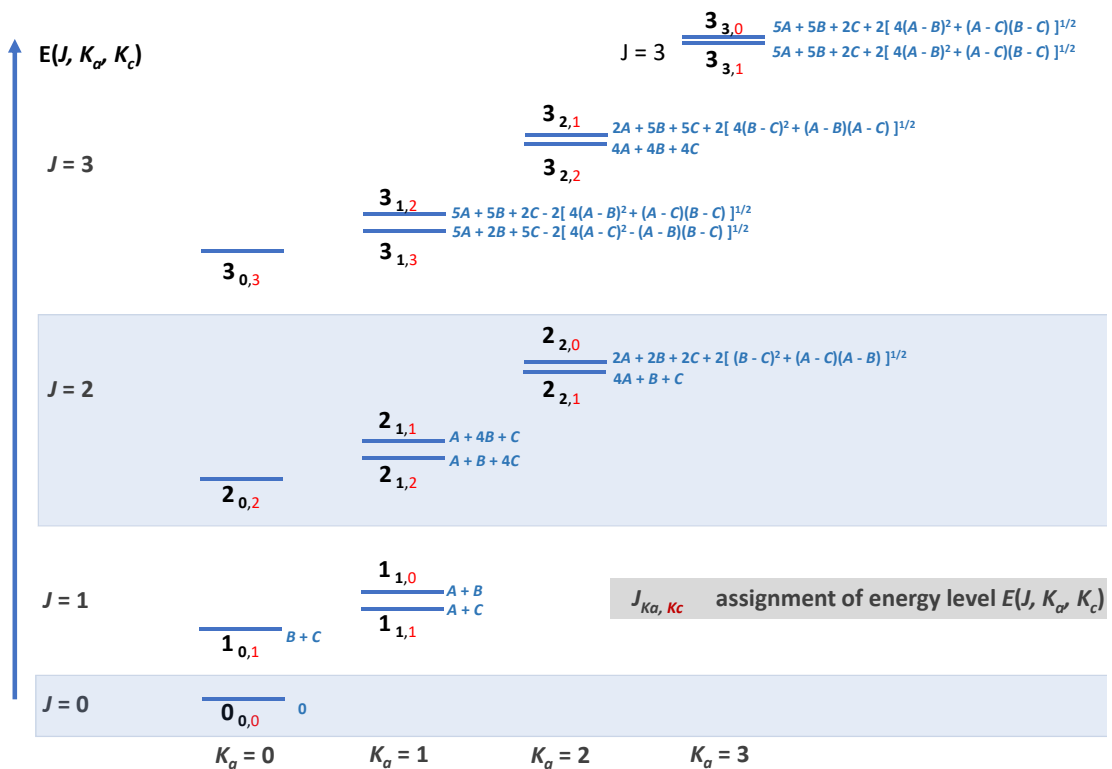
- 2) The rotation is governed by the total angular momentum J , with projections: J_a, J_b, J_c

- 3) The QM rotational energy of a rigid molecule is given by the stationary Schrödinger Equation:

$$\hat{H}\Psi(J, K_a, K_c) = E\Psi(J, K_a, K_c) \quad K_a, K_c \text{ projection quantum numbers of } J \text{ onto } a \text{ and } c \text{-axis}$$

$$\hat{H} = A \hat{J}_a^2 + B \hat{J}_b^2 + C \hat{J}_c^2 \quad \text{and} \quad A = \frac{\hbar^2}{2I_a} \quad B = \frac{\hbar^2}{2I_b} \quad C = \frac{\hbar^2}{2I_c}$$

- 4) Solving the Schrödinger Eq. leads to rotational energy levels $E(J, K_a, K_c) = E(A, B, C)$ of a rigid molecule. PGopher calculates energy levels for given rotational constants A, B, C .



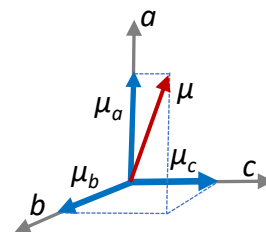
5) Rotational spectra of molecules.

Non-zero dipole components μ_a , μ_b , μ_c along the principal axes a , b , c generate rotational spectra according to dipole selection rules:

$$a\text{-type } \Delta J = 0, \pm 1 \quad \Delta K_a = 0, (\pm 2) \quad \Delta K_c = \pm 1, (\pm 3)$$

$$b\text{-type } \Delta J = 0, \pm 1 \quad \Delta K_a = \pm 1, (\pm 3) \quad \Delta K_c = \pm 1, (\pm 3)$$

$$c\text{-type } \Delta J = 0, \pm 1 \quad \Delta K_a = \pm 1, (\pm 3) \quad \Delta K_c = 0, (\pm 2)$$



6) Rotational vibrational spectra

Vibration of a normal mode $v(q)$ in coordinate q with non-zero vibrational dipole components $\partial\mu_a/\partial q$, $\partial\mu_b/\partial q$, $\partial\mu_c/\partial q$ generate ro-vibrational spectra according to selection rules:

$$a\text{-type } \Delta v(q) = 1 \quad \Delta J = 0, \pm 1 \quad \Delta K_a = 0, (\pm 2) \quad \Delta K_c = \pm 1, (\pm 3)$$

$$b\text{-type } \Delta v(q) = 1 \quad \Delta J = 0, \pm 1 \quad \Delta K_a = \pm 1, (\pm 3) \quad \Delta K_c = \pm 1, (\pm 3)$$

$$c\text{-type } \Delta v(q) = 1 \quad \Delta J = 0, \pm 1 \quad \Delta K_a = \pm 1, (\pm 3) \quad \Delta K_c = 0, (\pm 2)$$

7) Quantum numbers to label transitions

The allowed transitions between energy levels form a spectrum, which shows characteristic groups of transitions, called **branches**.

P-branches have $\Delta J = -1$, **Q-branches** have $\Delta J = 0$, **R-branches** have $\Delta J = +1$

Transitions between K quantum numbers (ΔK) are set as a superscript to the name of the branch. The lower K quantum number is given as a subscript:

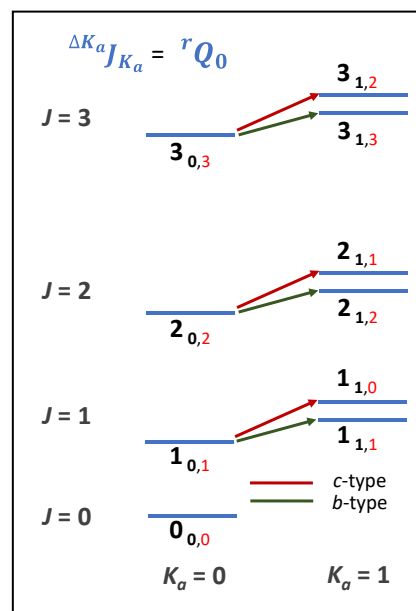
ΔK	J_K	p for $\Delta K = -1$,
		q for $\Delta K = 0$,
		r for $\Delta K = +1$

e.g., ${}^r Q_0$ branch transitions

$$(J, k_a=0, k_c) \rightarrow (J, K_a=1, K_c')$$

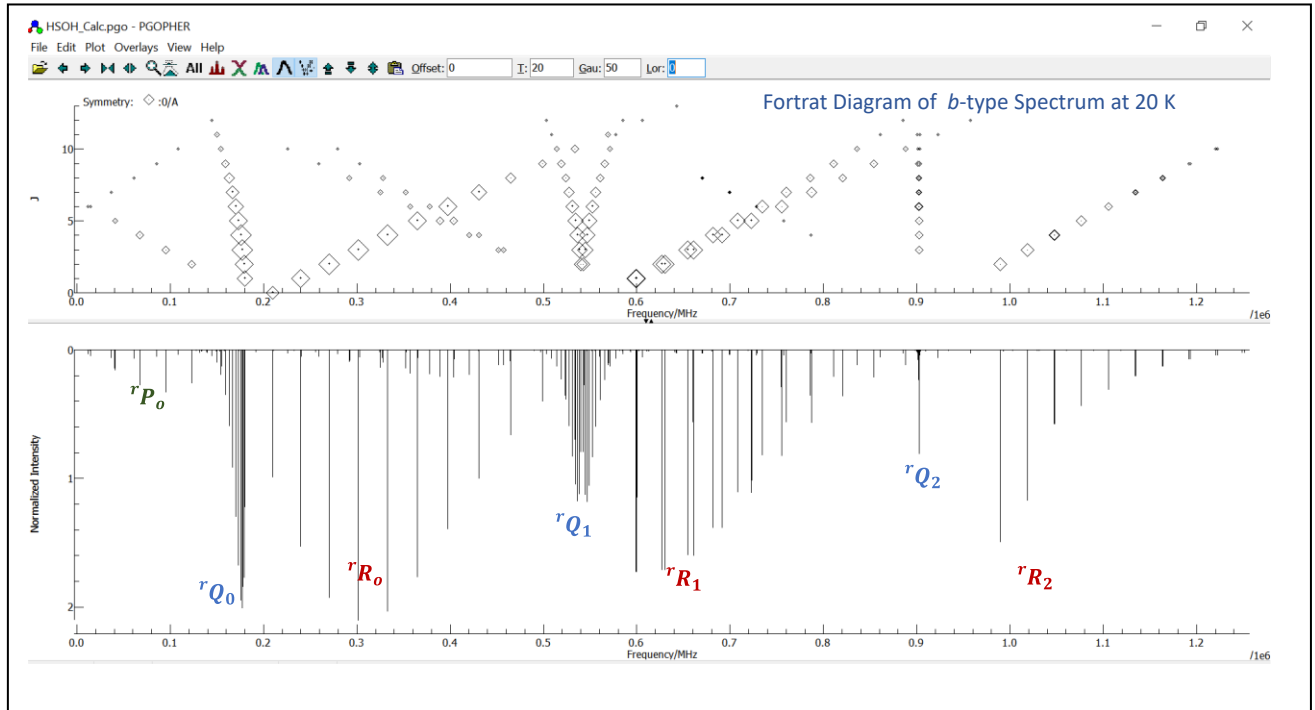
Note: There are b - and c -type transitions for ${}^r Q_0$

In case on non-zero dipole components along the b - and c -axis.



8) Fortrat Diagram

The plot shows a calculated spectrum of HSOH at low temperatures with some strong Q- and R-branches and weaker P-branches. The structure of a spectrum is best presented in a Fortrat diagram, where the frequency of the transitions are plotted versus the J quantum number. Fortrat diagrams are useful tools to assign spectral lines.



9) Infrared rotational vibrational spectra.

According to vibrational dipole selection rules (see Par. 6) ro-vibrational transitions connect rotational energy levels of a lower vibrational state with those of an upper, vibrationally excited state. The A, B, C, rotational constants vary slightly with the vibrational quantum number, resulting in two sets of rotational constants, one for the lower state A_0, B_0, C_0 , and one for the upper vibrational state, A_1, B_1, C_1 . Both sets of rotational constants can be derived from the spectrum. For linear molecules only the $K_a = 0$ levels are present with B the only rotational constant.

Right: a-type transitions with P- and R-branches. Bottom: Ro-vibrational spectrum of a linear molecule.

