

Molecular Chirality:
Enantiomer Differentiation
by High-Resolution Spectroscopy

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Two “origins” of chirality

(1) Hund’s paradox (1927)

Hamiltonian symmetric, but enantiomers actually exist as stable molecules without any definite parity. Tunneling, but the splitting is negligibly small, making R and S remain as stable chiral molecules

(2) Parity violation (CP conserved, but P not) PV

T. D. Lee and C. N. Yang (1956) theory

K meson (θ , τ) decay

C. S. Wu et al. (1957) experiment on ^{60}Co

Parity violation

(1) *d*-,*l*-camphor

Arimondo, Glorieux, Oka (1977)
vibrational spectra, Lamb dip 10^{-8}

(2) CHFC1Br

Daussy, Marrel, Amy-Klein, Nguyen, Bordé,
Chardonnet (1999)

ν_4 band at $9.3 \mu\text{m}$, saturation dip 5 kHz

$\nu(R-)-\nu(S+) = 9.4 (\pm 5.1 \pm 12.7) \text{ Hz}$

$< 3.9 \times 10^{-13}$ (theory 10^{-16})

High-resolution spectroscopic studies of molecular chirality (continued)

Spectroscopic resolution 10^{-12} vs **PV**
 10^{-16}

CH_3ReOSSe large effects expected
[Optical lattice clocks 10^{-18} (H. Katori)]
Possibility of detection ?

No ! It is impossible !

This answer had been widely accepted until
2009.

Triple resonance for three rotational levels of a C_1 chiral molecule:

Not energy, but phase

2009 The 3rd Molecular Science Symposium at Nagoya University

2010 65th Ohio State Univ. International Symposium on Molecular Spectroscopy

Paper submitted around 2009, to *J. Chem. Phys.*, but not accepted !!! Five referees: Negative, except one !

The idea has been spread over through refereeing.

Then to *Proc. Jpn. Acad. Ser. B*, **68**, 120-128 (2012)

Chiral molecules of C_1 symmetry

R and S are assumed to be “stable”, namely

Hund's paradox: high potential barrier between enantiomers [*ex.* propylene oxide $\text{CH}_3\text{CH}(\text{O})\text{CH}_2$]

A typical asymmetric rotor:

three principal moments of inertia: $I_{aa} < I_{bb} < I_{cc}$

all the three components of the electric dipole moment: μ_a, μ_b, μ_c are finite.

There are numerous sets of three rotational states, which are connected by a -, b -, c -type transitions.

1_{10}



b



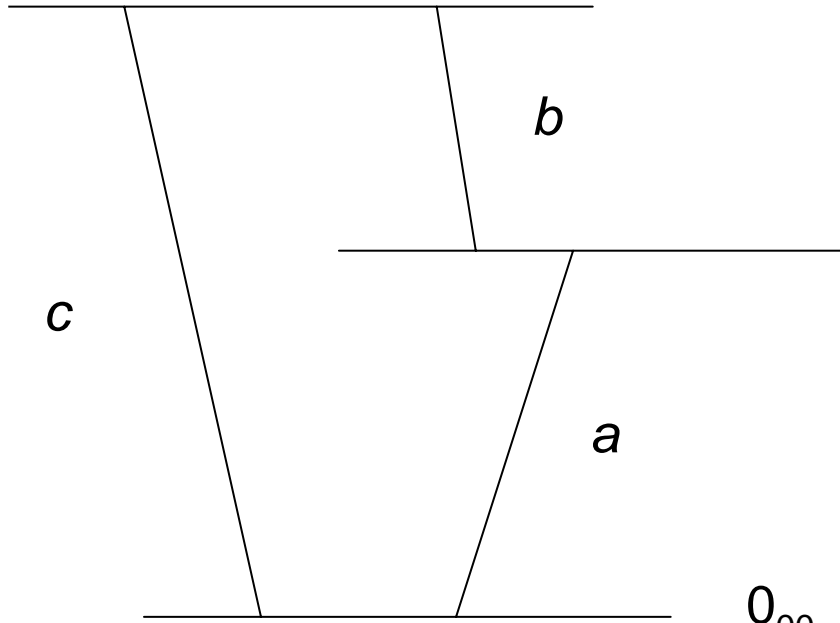
1_{01}

c

a



0_{00}

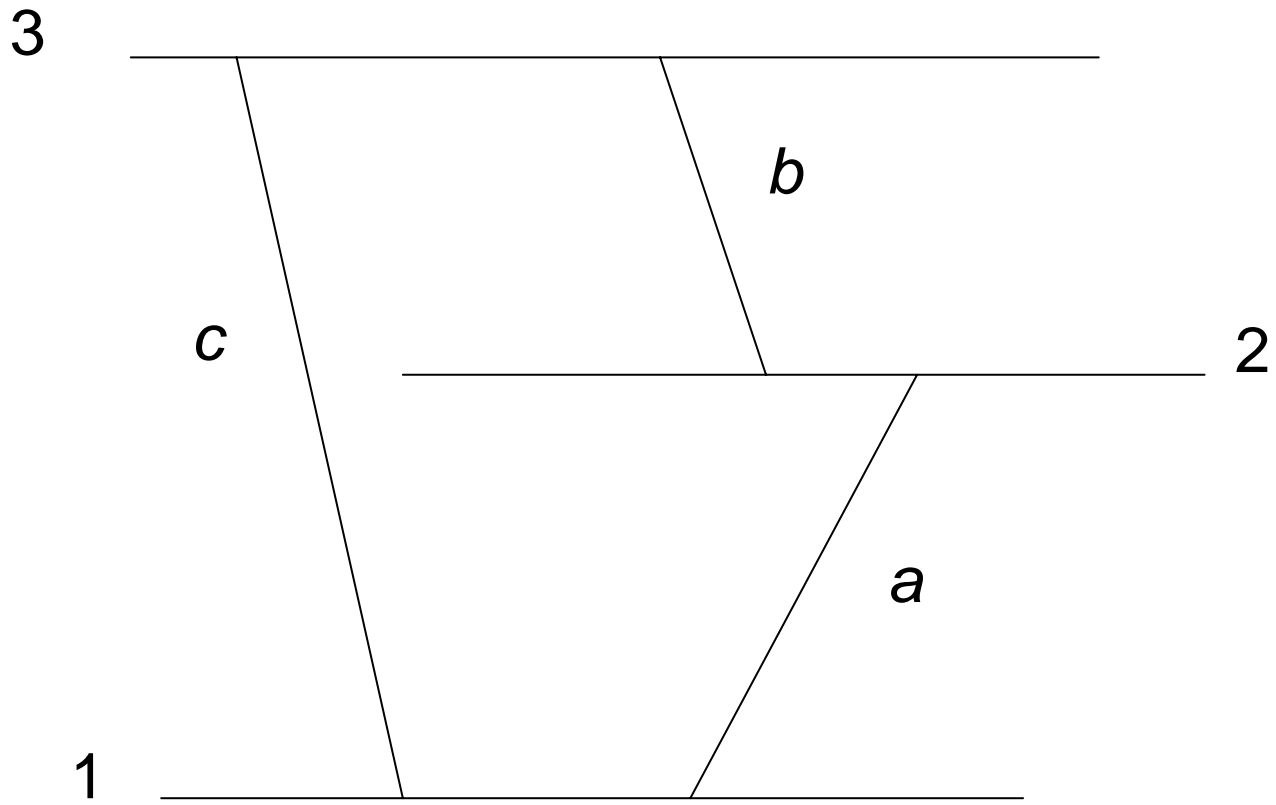


The present study is based upon
rotational spectroscopy

Molecular rotation in free space
mainly in microwave region

Rotational transitions take place
through the interaction of a
permanent (electric) dipole moment
with the microwave (electric) field.

Parity + \leftrightarrow -



Three rotational level system

Three-level system (1)

Triple resonance by time-dependent perturbation

$$i\hbar \partial \psi / \partial t = (\mathbf{H}_0 + V(t)) \psi$$

$$V(t) = \sum_g [F_g \exp(-i \omega_g t) + G_g \exp(i \omega_g t)]$$

$$g = a, b, c; \quad (G_g)_{nm} = (F_g)_{mn}^*$$

$$\psi = \sum_k a_k(t) \psi_k^{(0)}, \quad \psi_k^{(0)}: k\text{-th stationary state}$$

$$i\hbar da_k/dt = \sum_n V_{kn}(t) a_n(t),$$

$$V_{kn}(t) = \sum_g \{ (F_g)_{kn} \exp[i(\omega_{kn} - \omega_g)t] \\ + (F_g)_{nk}^* \exp[i(\omega_{kn} + \omega_g)t] \}$$

$$(F_g)_{kn}: \text{Stark effect matrix element}$$

Three-level system (2)

Nonresonant terms are neglected.

$$i\hbar da_1/dt = F_{21}^* \exp(-i \varepsilon_a t) a_2 + F_{31}^* \exp(-i \varepsilon_c t) a_3$$

$$i\hbar da_2/dt = F_{21} \exp(i \varepsilon_a t) a_1 + F_{32}^* \exp(-i \varepsilon_b t) a_3$$

$$i\hbar da_3/dt = F_{31} \exp(i \varepsilon_c t) a_1 + F_{32} \exp(i \varepsilon_b t) a_2$$

$$\omega_{21} = \omega_a + \varepsilon_a, \quad \omega_{31} = \omega_b + \varepsilon_b,$$

$$\omega_{32} = \omega_c + \varepsilon_c,$$

Exact resonance $\varepsilon = 0$ assumed

Conditions for the coefficients

$$d^3 a_1 / dt^3 + [(F_{21}^* F_{21} + F_{31}^* F_{31} + F_{32}^* F_{32}) / \hbar^2] da_1 / dt - i[(F_{31}^* F_{32} F_{21} + F_{21}^* F_{32}^* F_{31}) / \hbar^3] a_1 = 0$$

A trial function for a_1 : $a_1 = A_1 \exp(i \lambda t)$

$$\lambda^3 - D_2^2 \lambda + D_3^3 = 0$$

$$D_2^2 = (|F_{21}|^2 + |F_{31}|^2 + |F_{32}|^2) / \hbar^2$$

$$D_3^3 = (F_{31}^* F_{32} F_{21} + F_{31} F_{32}^* F_{21}^*) / \hbar^3$$

Time-dependent eigenfunction

$$\begin{aligned}\psi(t) = & A_1[\psi_1^{(0)}(t) + C_{21}\psi_2^{(0)}(t) + C_{31}\psi_3^{(0)}(t)] \\ & \times \exp(i\lambda_1 t) \\ & + A_2[\psi_1^{(0)}(t) + C_{22}\psi_2^{(0)}(t) + C_{32}\psi_3^{(0)}(t)] \\ & \times \exp(i\lambda_2 t) \\ & + A_3[\psi_1^{(0)}(t) + C_{23}\psi_2^{(0)}(t) + C_{33}\psi_3^{(0)}(t)] \\ & \times \exp(i\lambda_3 t)\end{aligned}$$

$$C_{2i} = [\lambda_i F_{21} - F_{32}^* F_{31} / \hbar] / \hbar / [-\lambda_i^2 + |F_{32}|^2 / \hbar^2]$$

$$C_{3i} = [\lambda_i F_{31} - F_{32} F_{21} / \hbar] / \hbar / [-\lambda_i^2 + |F_{32}|^2 / \hbar^2]$$

Initial conditions:

at $t = 0$, the system lies in the level 1

$$A_1 + A_2 + A_3 = 1, \quad A_1 C_{21} + A_2 C_{22} + A_3 C_{23} = 0,$$

$$A_1 C_{31} + A_2 C_{32} + A_3 C_{33} = 0.$$

$$A_1 = \varrho_1(\lambda_2 - \lambda_3)/\Lambda, \quad \varrho_1 = -\lambda_1^2 + \lambda_0^2,$$

$$A_2 = \varrho_2(\lambda_3 - \lambda_1)/\Lambda, \quad \varrho_2 = -\lambda_2^2 + \lambda_0^2,$$

$$A_3 = \varrho_3(\lambda_1 - \lambda_2)/\Lambda, \quad \varrho_3 = -\lambda_3^2 + \lambda_0^2,$$

$$\begin{aligned} \Lambda = & \lambda_1 \lambda_2 (-\lambda_1 + \lambda_2) + \lambda_2 \lambda_3 (-\lambda_2 + \lambda_3) \\ & + \lambda_3 \lambda_1 (-\lambda_3 + \lambda_1) \end{aligned}$$

$$\lambda_0^2 = |F_{32}|^2 / \hbar^2$$

Transition probability

$$\begin{aligned} W_{2-1} &= |A_1 C_{21} \exp(i \lambda_1 t) + A_2 C_{22} \exp(i \lambda_2 t) \\ &\quad + A_3 C_{23} \exp(i \lambda_3 t)|^2 \\ &= (1/L^2) \{ (\lambda_2 - \lambda_3)^2 (P_1^2 + Q_1^2) \\ &\quad + (\lambda_3 - \lambda_1)^2 (P_2^2 + Q_2^2) + (\lambda_1 - \lambda_2)^2 (P_3^2 + Q_3^2) \\ &\quad + 2(\lambda_2 - \lambda_3)(\lambda_3 - \lambda_1) [(P_1 P_2 + Q_1 Q_2) \cos(\lambda_1 - \lambda_2)t \\ &\quad \quad + (P_1 Q_2 - P_2 Q_1) \sin(\lambda_1 - \lambda_2)t] \\ &\quad + 2(\lambda_3 - \lambda_1)(\lambda_1 - \lambda_2) [(P_2 P_3 + Q_2 Q_3) \cos(\lambda_2 - \lambda_3)t \\ &\quad \quad + (P_2 Q_3 - P_3 Q_2) \sin(\lambda_2 - \lambda_3)t] \\ &\quad + 2(\lambda_1 - \lambda_2)(\lambda_2 - \lambda_3) [(P_3 P_1 + Q_3 Q_1) \cos(\lambda_3 - \lambda_1)t \\ &\quad \quad + (P_3 Q_1 - P_1 Q_3) \sin(\lambda_3 - \lambda_1)t] \} \end{aligned}$$

Experimental realization

- (1) D. Patterson, M. Schnell, and J. M. Doyle, *Nature* **497**, 475-478 (2013).
- (2) D. Patterson and J. M. Doyle, *Phys. Rev. Lett.* **111**, 023008 (2013).
- (3) V. Alvin Shubert, D. Schmitz, D. Patterson, J. M. Doyle, and M. Schnell, *Angew. Chem. Int. Ed.* **53**, 1152 (2014).

1,2-propanediol, 1,3-butanediol, carvone

- (1) Stark switching
- (2) simultaneous identification of species and handedness

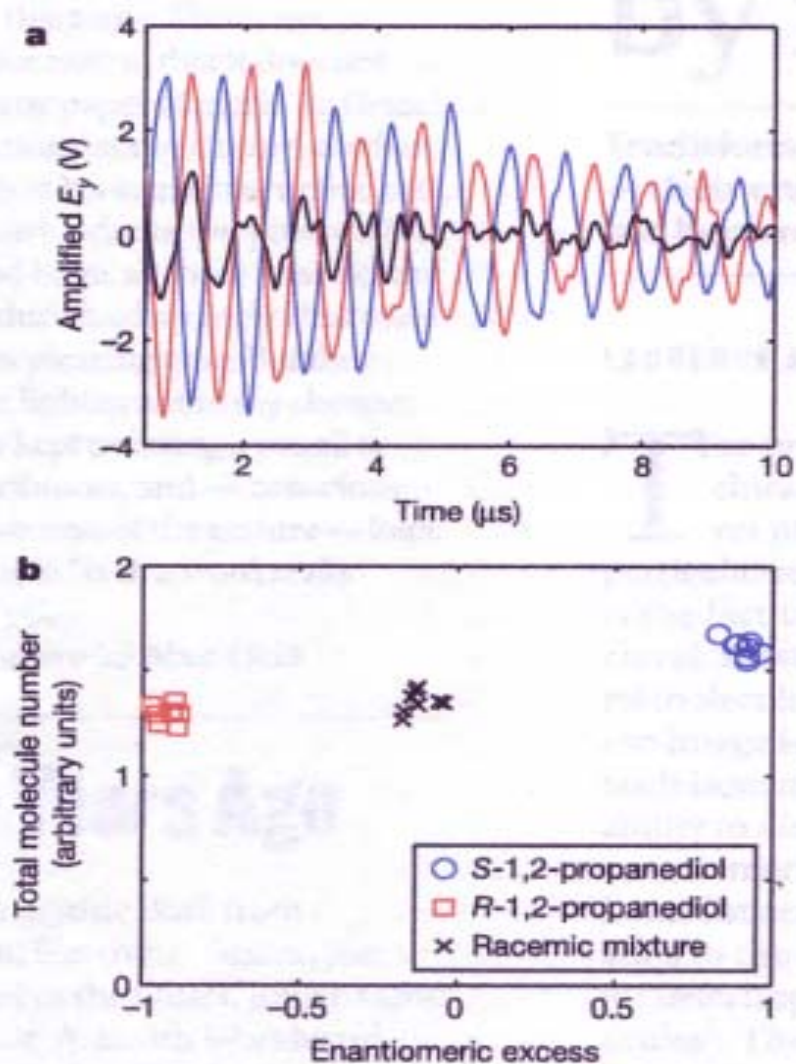


Figure 4 | Enantiomer-dependent microwave radiation. **a**, The enantiomer dependent free-induction decay traces for *S*-1,2-propanediol (blue trace), *R*-1,2-propanediol (red) and racemic 1,2-propanediol (black). As predicted, opposite enantiomers show a 180° phase difference. **b**, Repeated measurements enantiomeric excess (horizontal axis) and of total molecule number (vertical axis) for *S*-, *R*- and racemic 1,2-propanediol. Each data point represents about 20 s experimental time, and 1 mg of sample. Enantiomers are clearly resolved.

A new potential method for the study of molecular chirality

Microwave spectroscopy vs polarimeter

MW based on a completely new principle
rotational spectra, only in the **gaseous
phase**, i.e. complementary to
polarimeter

much more superior in

**sensitivity, resolution, accuracy,
and so on**

Biomolecules and others

Recent examples of the MW studies:

J. L. Alonso, Univ. Valladolid, Spain

neurotransmitters, glucose, etc.

aspirin, cytosine, vitamine C,
dopamine, octopamine, serotonin,
synephrine

Y. Kawashima, Kanagawa Inst. Tech.

whisky lactone

1. Chiral molecules of C_2 and C_n ($n \geq 3$) symmetry

C_2 symmetry (ex. CHF=C=CHF)

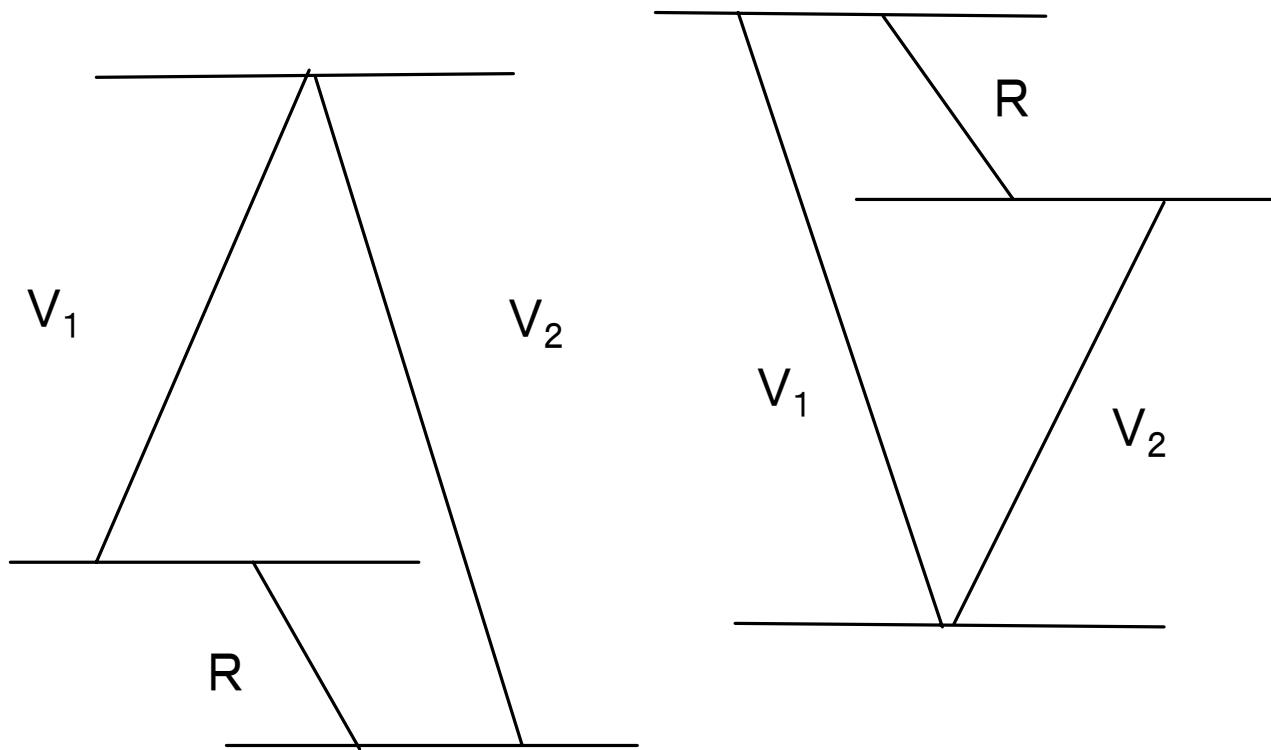
C_n ($n \geq 3$) symmetry symmetric top
(ex. Sumanene)

electric dipole moment aligned to the C_2 or C_n axis only, therefore no three-level systems exist within one vibronic state.

But ...

励起状态
Excited state

基底状态
Ground state



2. Racemization

Equal amount of enantiomers
racemization processes

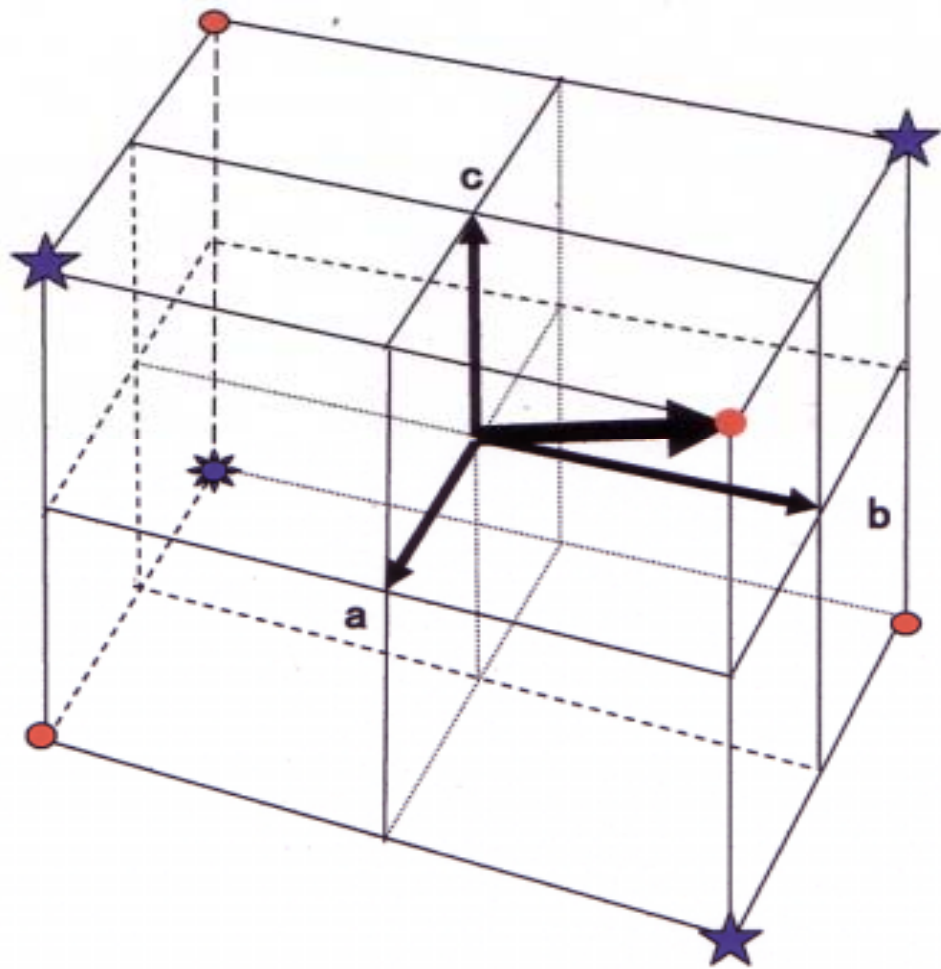
to be explained on **molecular basis**

(Relations to Hund's tunneling processes ?)

Transitions between **mirror** images

[Changes of chemical bonds involving the
asymmetry atoms (carbons)]

Reflection: $U_a \sigma_{bc} + U_b \sigma_{ca} + U_c \sigma_{ab}$
($U_a + U_b + U_c = 1.0$)



3. Rotational isomers

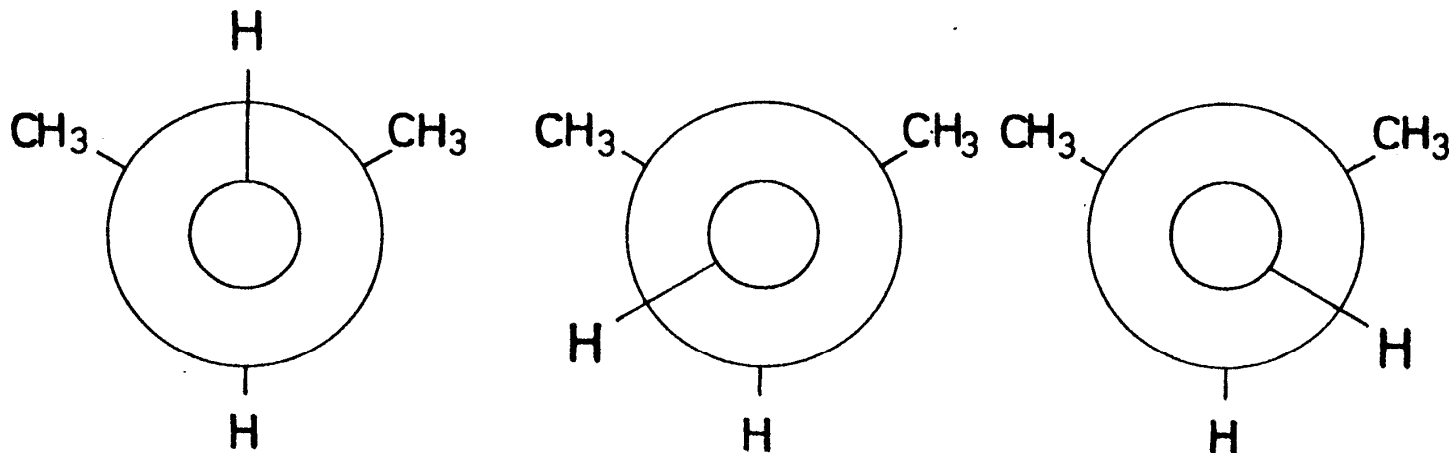
Gauche

not classified as chiral molecules,
but two gauche forms are mirror
images, *i.e.* chiral !

At temperatures as low as a few K,
the barrier between them is **high**.

Isopropyl alcohol

$(\text{CH}_3)_2\text{CHOH}$



Trans Form

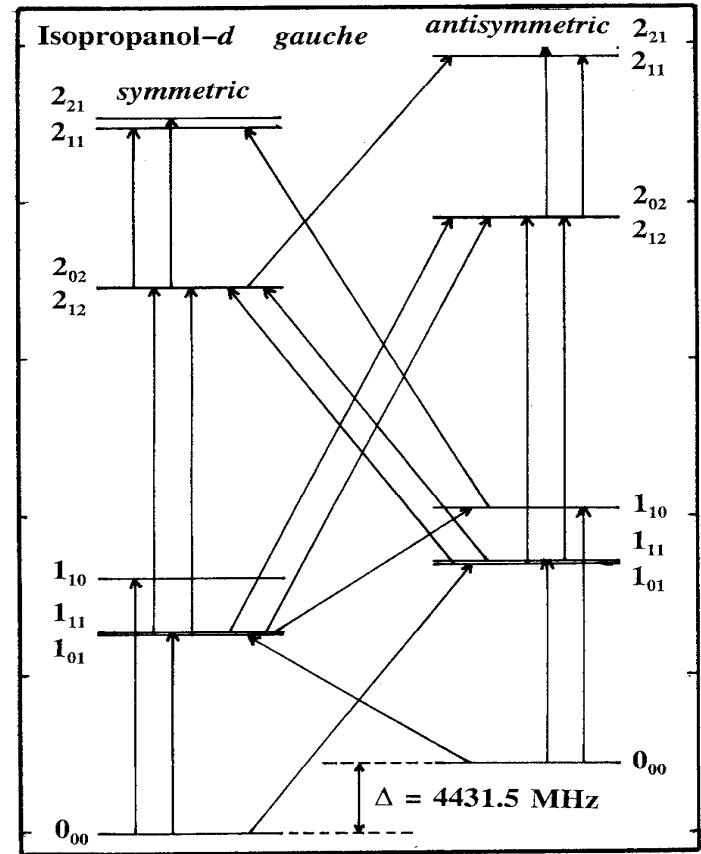
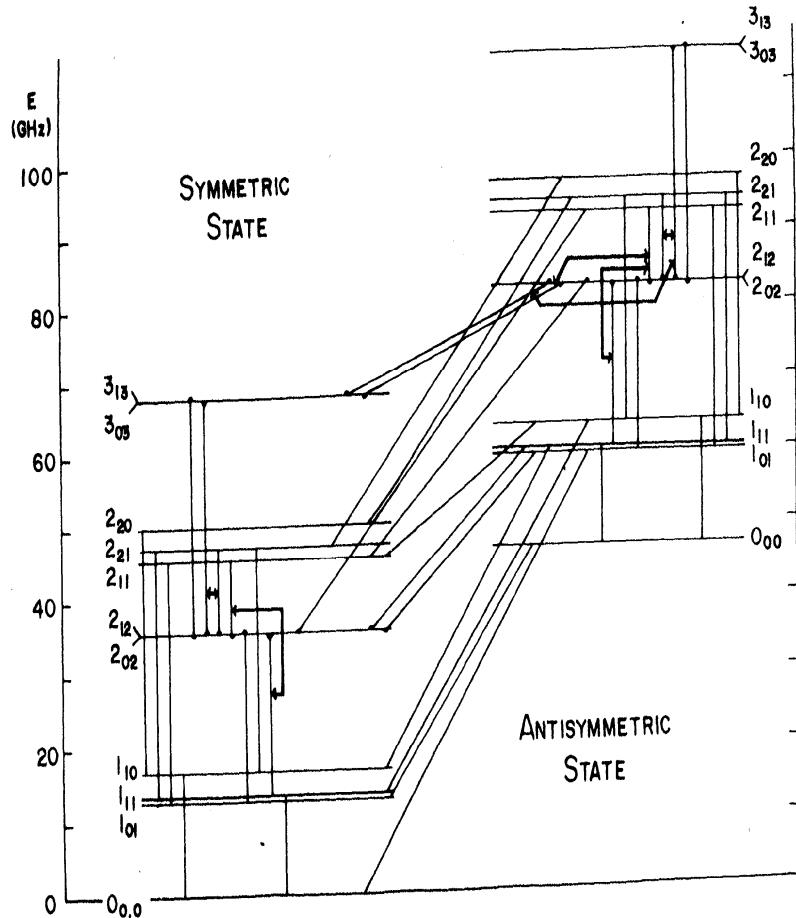
Gauche Form

FIG. 1. Schematic diagram of rotational isomers of isopropyl alcohol

Isopropanol *gauche* energy levels

normal

OD-species



Effective Hamiltonian for **gauche** form of isopropanol

$$H_{ss} = - \Delta/2 + A_s J_x^2 + B_s J_y^2 + C_s J_z^2 + \text{centrifugal terms}$$

$$H_{aa} = + \Delta/2 + A_a J_x^2 + B_a J_y^2 + C_a J_z^2 + \text{centrifugal terms}$$

$$H_{sa} = - iQ_y J_y - iQ_z J_z + (R_{zx}/2)(J_z J_x + J_x J_z) \\ + (R_{xy}/2)(J_x J_y + J_y J_x) + \dots$$

$$H_{as} = H_{sa}^*$$

$$\Delta = 46798.901(60) \text{ [OH] MHz}$$

$$4431.4613(17) \text{ [OD] MHz } [\sim 2400]$$

OH: E. Hirota, *J. Phys. Chem.* **83**, 1457 (1979)

OD: E. Hirota and Y. Kawashima, *J. Mol. Spectrosc.* **207**, 243 (2001)