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SEVENTH COLLEGE ON BIOPHYSICS:

*Structure and Function of Biopolymers: Experimental and Theoretical
Techniques.*

4 - 29 March 1996

*Fundamental Symmetry Principles in Relation to the Physical-
Chemical Foundations of Molecular Chirality and Possible Biological
Consequences*

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Fundamental Symmetry Principles
in Relation to the Physical-Chemical
Foundations of Molecular Chirality
and Possible Biological Consequences

Martin Quack
ETH Zürich

Mini symposium on

Asymmetry in Biomolecules
and
Dissymmetry in Biomolecules
or
Chirality in Biomolecules

Trieste March 1996

M.Q. -1-

Physical-Chemical Foundations of the
Structure and Dynamics of
Chiral Molecules

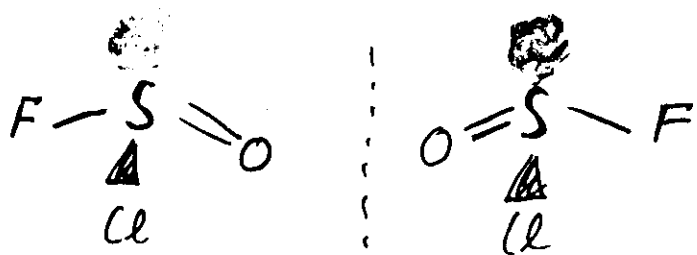
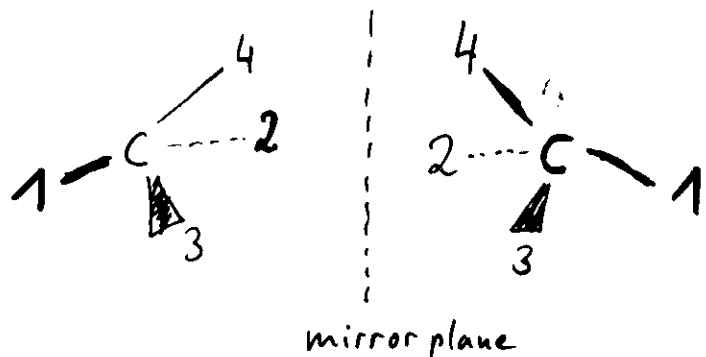
1. What is molecular chirality?
2. Why at all? → Symmetry!
3. Brief history of chirality
4. Hypotheses on chirality today
"Communities of belief"
5. De facto and de lege symmetry breaking
6. Control of Stereomutation
by Femtosecond Lasers
7. Parity violating molecular potentials
Theory and proposed experiments
8. Time reversal symmetry and
molecular irreversibility
Test of CPT in chiral molecules+Speculations

M.Q. -2-

What is molecular chirality?

Assume

4 different particles
(atoms, nuclei in molecules)



Pyramidal sulfoxides

Non planar: Always chiral as
image and mirror image
or idealized left and right hand

$\chi_{\text{Cl}}^{\ominus}$ = the hand (Kelvin ~ 1900)
M.O. - 3 -

N.O. - 4 -

Figure 1

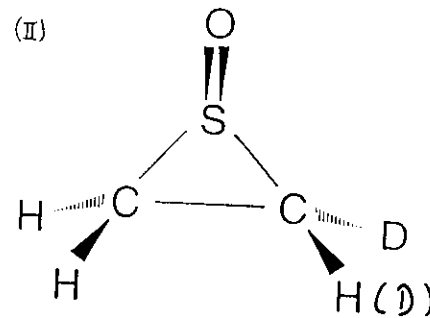
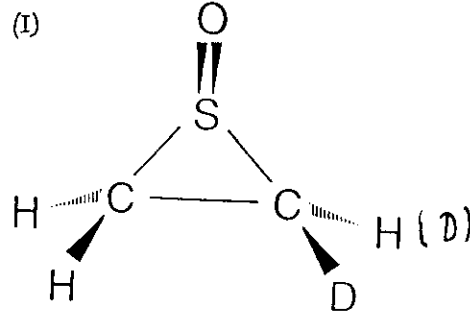


Figure 1

(III)

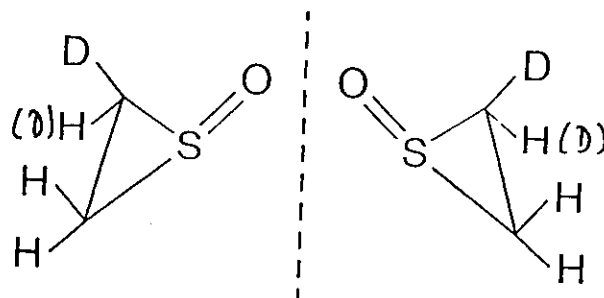


Fig 1 Crisp, He, Jentner, Black, Seyfang

R. Marquardt, M. Quack, J. Stohner and E. Sutcliffe

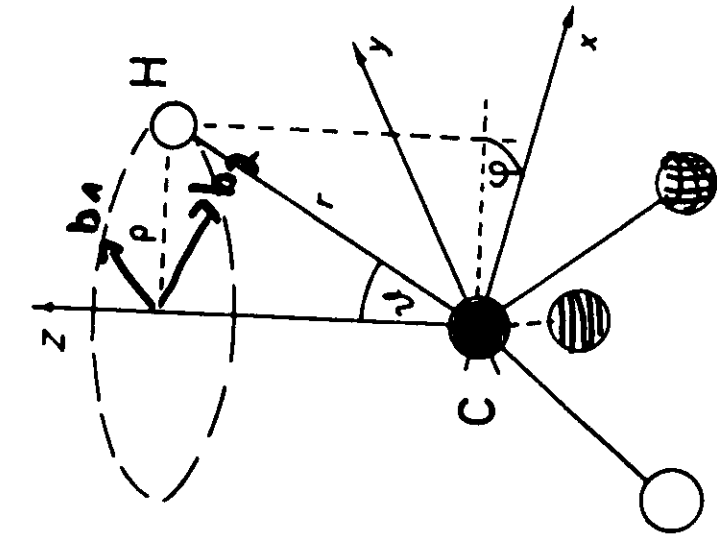
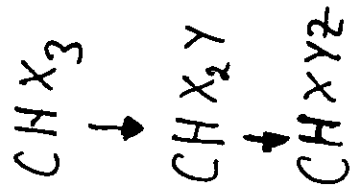
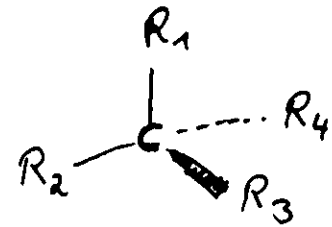
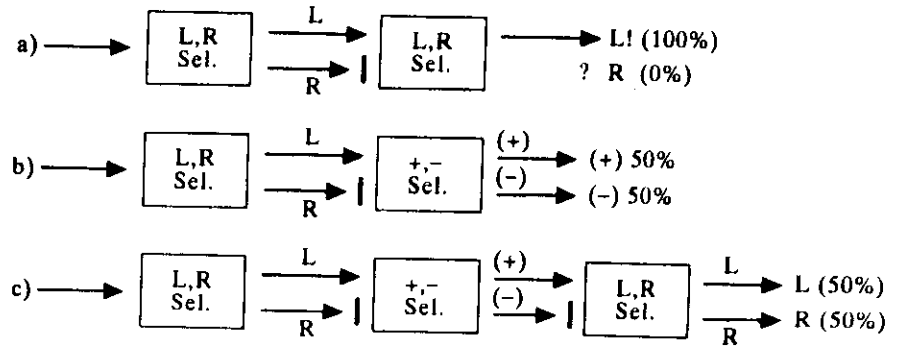


Fig. 1. Coordinates for the CH chromophore in X_3CH compounds.

Symmetry
Reduction



1989/2001 ? M.Q. - 6 -
(M.Q. Angew. Chem. Int. Ed. 1987)



There are not just two isomers
 ("R" and "S" or "D" and "L")

But there are 4 Isomers

"D", "L", "+", "-"

or

R, S, P, M

M.Q-7-

The Symmetry of Time and Space in Molecular Processes

1. Mirror (left-right) symmetry
Space Inversion Symmetry
Violated in the daily "Life"
of the biochemist: Chirality
Preferred L-aminoacids in proteins

2. Time Reversal Symmetry
Reversibility of dynamical,
molecular processes

Violated in the daily "Life"
Irreversibility of chemical
and biochemical processes
giving rise to birth and death.

The true origin of these Symmetry Violations is not understood to date

Not because of a lack
of possible explanations

But because of too many
different, contradictory
explanations

M. Q. Phil. Trans. Roy. Soc. London A32 (1990) 203

Angew. Chem. 101 (1989) 588

Intern. Ed. Engl. 28, 571 (1989)

J. Mol. Struct. 292 (1993) 171

OR

The Parable of the rings

Lessing, Spinoza, Boccaccio // Dante, Augustinus
18th-century Nathan // Frederick II // Paradiso De Trinitate

M.Q-8-

M.Q. - 9 -

The Symmetries of Time and Space and their Violations
in Chiral Molecules and Molecular Processes

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Switzerland

Complete paper
has been distributed
as background
reading

Lecture presented 16 April 1993 at the International Symposium
"Conceptual Tools for Understanding Nature", Trieste,
Proceedings eds. G. Costa and M. Giorgi
To be published by World Scientific in "Science and Epistemology Seminar"

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International Symposium

CONCEPTUAL
TOOLS
FOR
UNDERSTANDING
NATURE
New Concepts and
Perspectives
in modern Chemistry
TRIESTE
16-17 April 1993



Conference Hall
Faculty of Sciences, Via Giorgieri, 1

International Symposium

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Molecular Spectra, Dynamics and Fundamental Symmetries

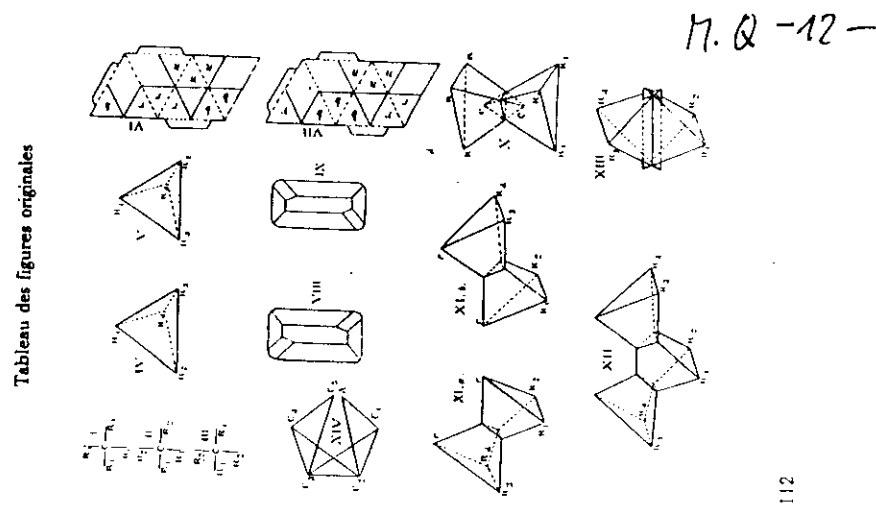
- (i) Translation in Space (\rightarrow Momentum)
- (ii) Translation in Time (\rightarrow Energy)
- (iii) Rotation in Space (Angular Momentum)
- (iv) Reflection in C.O.M. (Parity)
- (v) Time Reversal (Reversibility)
- (vi) Particle Permutation (Pauli - Symmetry)
- (vii) Charge conjugation (Matter - Symmetry with Antimatter)

The discrete symmetries
might all be violated!
De facto and de lege

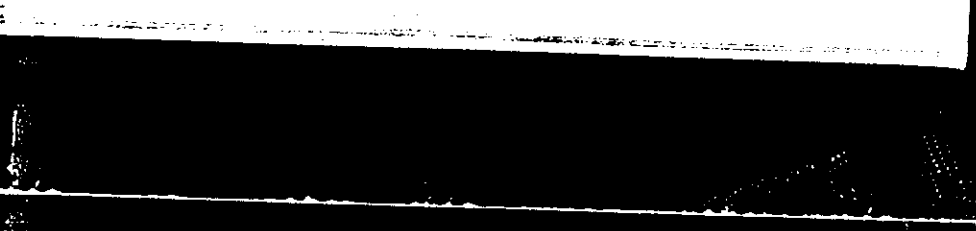
M.Q. - 10

Brief history of Chirality in Chemistry and Physics

1. Pasteur 1848 / 1860
"Dissymmetry" and Optical Activity
2. Le Bel + van't Hoff - 1874
spatial structure of (organic) carbon compounds → CIP 1956
3. Alfred Werner ~ 1900 - 1912
Chiral (inorganic) coordination compounds
Kelvin (~ 1900) Name "Chiral"
4. Friedrich Hund 1927: Parity
Quantum mechanics of chiral molecules
5. Bijvoet (1952) absolute chiral structure
6. Yang and Lee (Wu) 1956/57
 β -decay and chirality, Parity V.
Glashow, Salam, Weinberg ~ 1970
Electroweak theory, "chiral" Neutrino
7. Mason Tranter (1983), Quade (1980-86)
Theora \downarrow Exper.
N.A - 11 -



56 T 120



1887

LA CHIMIE DANS L'ESPACE
DIX ANNÉES DANS L'HISTOIRE D'UNE THÉORIE
par
J. H. VAN'T HOFF
À J. A. LE BEL,
En témoignage de ma respectueuse
affection
PRÉFACE*

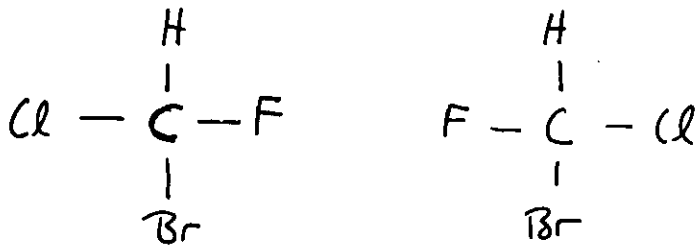
L'édition de ma brochure *La Chimie dans l'espace* étant épuisée, j'ai conçu le projet de publier, comme deuxième édition, le présent travail.
On y retrouvera par conséquent l'exposé primitif des idées dont il s'agissait; seulement, grâce aux travaux de plusieurs chimistes, il y a eu à ajouter un aperçu déjà assez important des vérifications que ces idées ont reçu dans les dix années écoulées depuis leur naissance.

* L'édition originale de cet opuscule (P. M. Barendijk, éd., Rotterdam, 1887), comporte un certain nombre de fautes d'impression évitées dans cette édition. Par ailleurs le français de Van't Hoff, comme on le verra, est parfois loin d'être correct, mais dans la mesure où il reste toujours compréhensible, nous avons voulu laisser ce monument en l'état. Pour des raisons de pagination, les références citées en notes ont été énumérées à la suite (on notera, à ce propos, que *Berl. Ber.* signifie *Berichte der deutschen chemischen Gesellschaft*). Les citations en allemand ont été traduites par le préfacier. (Note de J. Jacques.)

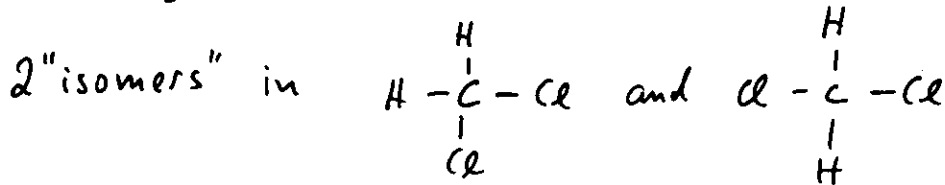
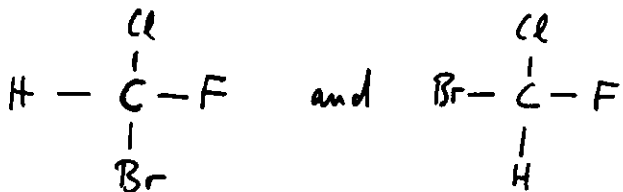
Simplistic structural views

Before 1873

Pre - Le Bel and van't Hoff

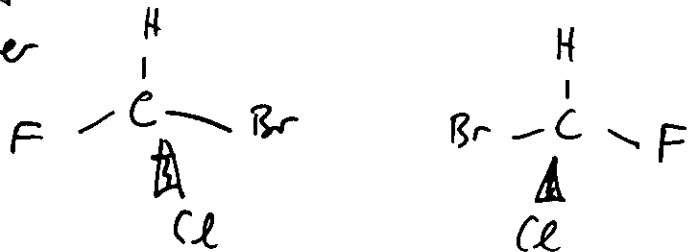


Same molecule, but "isomers"



1874

and after



just two mirror image isomers

N. Q. 13 -

[E_L = E_R] : van't Hoff 1897/1887

chimique (101), les conditions auxquelles un tel état de stabilité est assujéti. Il s'agit en effet d'une question de cet ordre : étant donné l'existence des deux isomères à pouvoir rotatoire opposé et la possibilité de leur transformation mutuelle, il s'agit de connaître les quantités relatives dans lesquelles ces deux composés doivent être en présence l'un de l'autre afin de former un système stable.

Un tel équilibre dépend du travail (E) que la transformation peut produire, travail qui doit être égal à zéro dans le cas en question, vu la symétrie mécanique parfaite des deux isomères, dont il s'agit, d'après la conception développée.

Il en résulte que la constante d'équilibre (K), qui détermine la proportion relative des deux composés, est égale à l'unité, parce que cette constante est reliée au travail (E) par l'équation suivante :

$$|K = -\frac{E}{RT}$$

où T indique la température absolue*. Il est clair alors que pour qu'il y ait équilibre les quantités relatives des deux isomères doivent être égales.

A cette même conclusion l'on arrive en envisageant le problème du côté dynamique (102) : la tendance de transformation étant la même chez les deux isomères, vu leur symétrie mécanique parfaite, tant que l'un d'eux prédomine, il s'en transformera une plus forte portion.

DEUXIÈME PARTIE

LA LIAISON SIMPLE DU CARBONE

I. APPLICATION DE L'IDÉE FONDAMENTALE.

Position relative des six groupes combinés en cas de liaison simple du carbone. En vue du développement de la théorie exposée il s'agit d'avoir une conception nette sur la structure des corps dans lesquels les atomes de carbone sont combinés à ce qu'on appelle la liaison simple. Le principe fondamental du groupement tétraédrique exige à lui seul que les deux atomes de carbone en question occuperont en même temps le centre de l'un des tétraèdres et le sommet de l'autre. Cette condition conduira par conséquent à la position relative des deux tétraèdres comme l'indique la figure 10 pour le composé C(R)₂C(R)₂, mais toute position relative différente, dérivant de celle-ci par rotation de l'un des tétraèdres autour de l'axe CC, serait également admissible.

Pour échapper à cette prévision d'une isométrie sans fin qui se présente ainsi au premier abord, il n'est nullement nécessaire d'introduire d'hypothèse additionnelle ; la difficulté disparaît d'un seul coup en tenant compte de l'action mutuelle que doivent exercer les groupes R et les groupes R', unis à chacun des deux atomes de carbone combinés. En effet, si cette action dépend, comme d'ailleurs toute force connue, de la distance et de la nature des groupes en question, il n'y aura parmi les positions possibles qu'une seule qui corresponde à l'état de stabilité. Comme telle nous

101. Van't Hoff, *Archives Néerl.* 1886. Kon. Svenska. Akad. Handl. 1886.
* La formulation actuelle de cette équation serait $|K = \frac{\Delta G}{RT}$.
102. Van't Hoff, *Ber. Ber.* X, 1670.

$\frac{\Delta G}{RT}$

N. Q. 14 -

Structure and Dynamics of Chiral Molecules**

By Martin Quack*

International Edition in English

28,571

1989

M.Q-15

(en Allemand:

vol. 101, 588

Could there be chiral methane? What is the characteristic structural feature (in a physicochemical sense) of a molecule? This question dates back to *Louis Pasteur*, the discoverer of molecular chirality, and since the work of *van 't Hoff* and *Le Bel* is generally considered by chemists as solved. In the present article it is pointed out that there exist fundamentally conflicting theoretical views of the physical origin of molecular chirality. These views predict consequences that could, in principle, be distinguished experimentally, but at present there is no conclusive experimental evidence available. Possible experiments are suggested that test different hypotheses. The importance of the magnitude of the parity-violating energy difference ΔE_{PV} in molecules due to the weak nuclear force for both the structure and spectra of chiral molecules and for the kinetics of racemization is discussed. The chemical relaxation rate coefficient of chiral molecules with some appreciable energy of excitation is derived for several limiting cases of a simple statistical mechanical model, which takes ΔE_{PV} into account.

*"Si les principes immédiats de la vie immédiate sont dissymétriques, c'est que, à leur élaboration, président des forces cosmiques dissymétriques; c'est là, suivant moi, un des liens entre la vie à la surface de la terre et le cosmos, c'est-à-dire l'ensemble des forces répandues dans l'univers". [***] L. Pasteur (19)*

1. Introduction

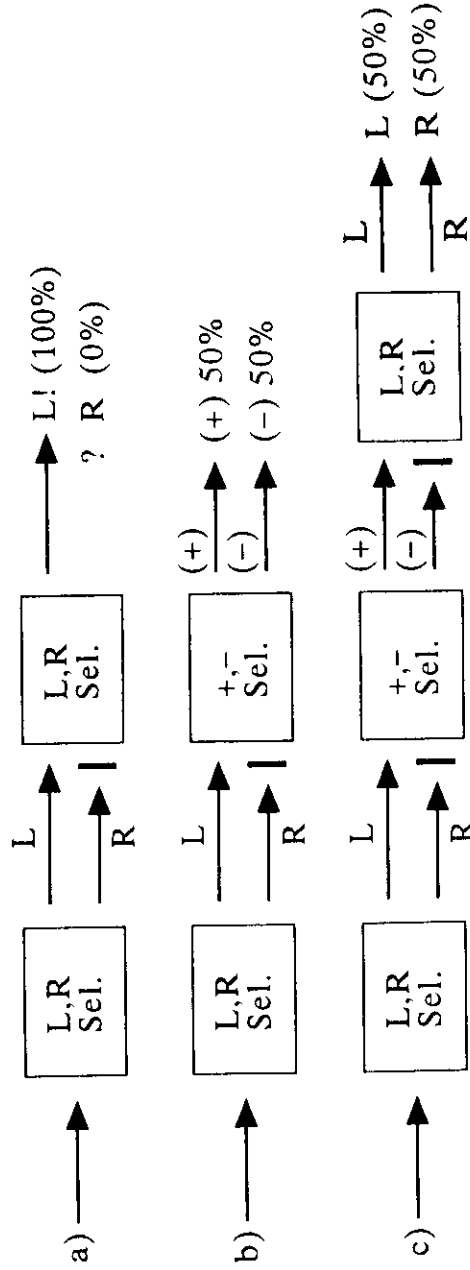
Since Pasteur's first separation of crystals of racemic organic compounds (such as the sodium ammonium salt of tartaric acid) into left- and right-handed, optically active compounds 140 years ago,⁽¹⁾ two major questions related to this observation of chirality have been addressed repeatedly:

1. What is the origin of chirality in *molecular physics* and thus the "nature" or intrinsic structural feature of a chiral molecule or chiral substance?
2. What is the origin of chirality in (molecular) *biology*? (i.e. the *chiral bias* favoring some enantiomers over others?)

PLUMIER, J. C. R. CHIRALITY 56 10127

stereochemistry.^[1,c.3,18-23] It was recognized by *Friedrich Hund*⁽²⁴⁾ that in the framework of quantum mechanics certain problems arise with classical stereochemistry due to the possibility of tunneling, which connects left- and right-handed structures. *Hund* provided an immediate apparent solution to these problems by considering the time scales for interconversion between enantiomers (see Section 2.2). *Priemas*⁽²⁵⁾ pointed out, however, that this solution does not explain, why one cannot buy in a drug store the substance corresponding to the coherent superposition of left- and right-handed states of chiral molecules such as alanine. Of course the reason for this may be trivial, the superposition

Surprising Experiment (suggested 1980)



M.Q-16

Communities of belief for M.Q.-17-
structural hypotheses of chiral molecules:
Consequences for Spectroscopy and dynamics
(M.Q. Angew. Chem. 1989)

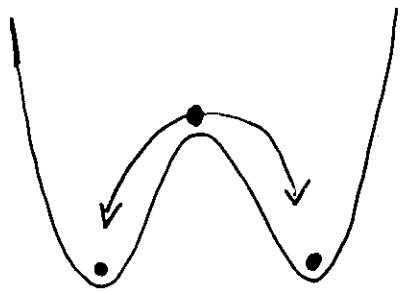
1. "Classical" hypothesis
van't Hoff and Le Bel 1887
Cahn, Ingold, Prelog 1956/66
2. F. Hund's hypothesis (1927)
3. "Perturbation" hypothesis
(Simonius, Harist Stodolsky 1978)
4. "Super selection rule" hypothesis
(Pfeifer, Primas 1980, A. Amann 1989f.)
5. Weak nuclear interaction and
parity violation
Lee and Yang (1956), Wu 1957
Mason + Tranter 1983 ff (calculations)
Quack 1980/86 (Proposed experiments)

Communities of Belief on M.Q.-18-
Chiral Biochemical Selection

1. Stochastic "all or nothing" selection
→ arbitrary D-L (e.g. Eigen 1971)
2. Accidental external, chiral influence
Many proposals since Pasteur
such as polarized light from sky,
crystalline matrix (quartz), β -radioactivity,
earth magnetic and other fields.....
3. Prebiotic (or abiotic) selection
by low T phase transition induced
by weak nuclear force (Salam, Chela Flores)
1991f
4. Predetermined selection of
preferred (more stable) enantiomer
by kinetic schemes including parity
violating energies (Kondeputi and Nelson
1985f.)

Spontaneous symmetry breaking

P.Q.-19-



"either" "or"

classically
"all or nothing"
same as de
facto symmetry
breaking

Quantum Mechanics (Ordinary Q.M.)

Superposition principle

"either, or" and as well as

by $|L, R\rangle = \frac{1}{\sqrt{2}} (| \text{either} \rangle \pm | \text{or} \rangle)$

Spontaneous symmetry breaking
in quantum mechanics removes

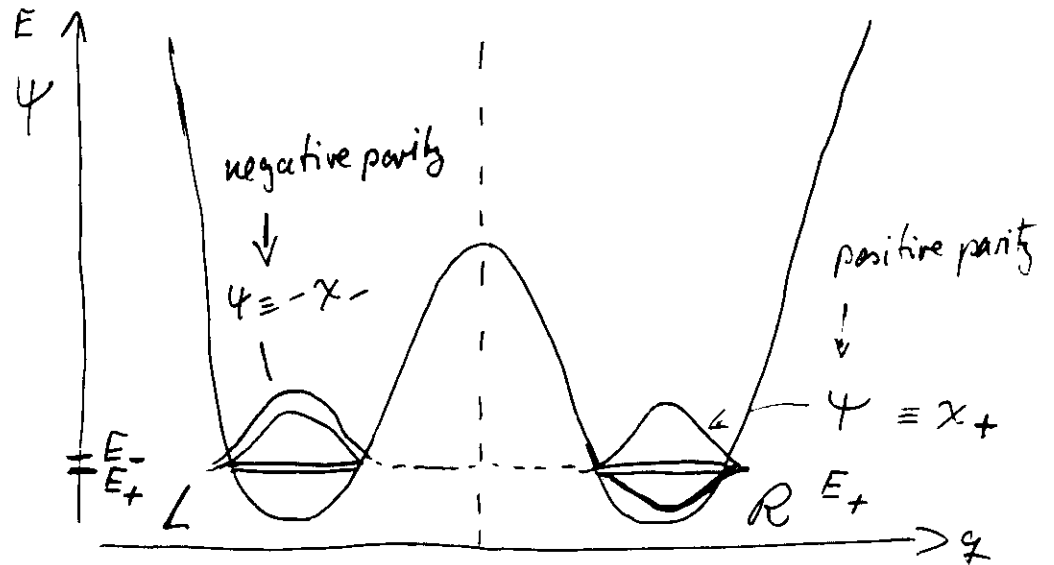
the "as well as" solution by
coupling to infinite numbers of d.o.f.

(radiation field etc.) \rightarrow classical properties
"either", "or" as in classical mechanics

De facto Symmetry breaking in quantum mechanics

P.Q.-20-

F.Hund 1927



Schematic: Symmetrical double minimum potential

"left" $\lambda = \frac{1}{\sqrt{2}} (\underline{x_+} - \underline{x_-})$

$\rho = \frac{1}{\sqrt{2}} (\underline{x_+} + \underline{x_-})$

$\Delta E_{\pm} = E_- - E_+$

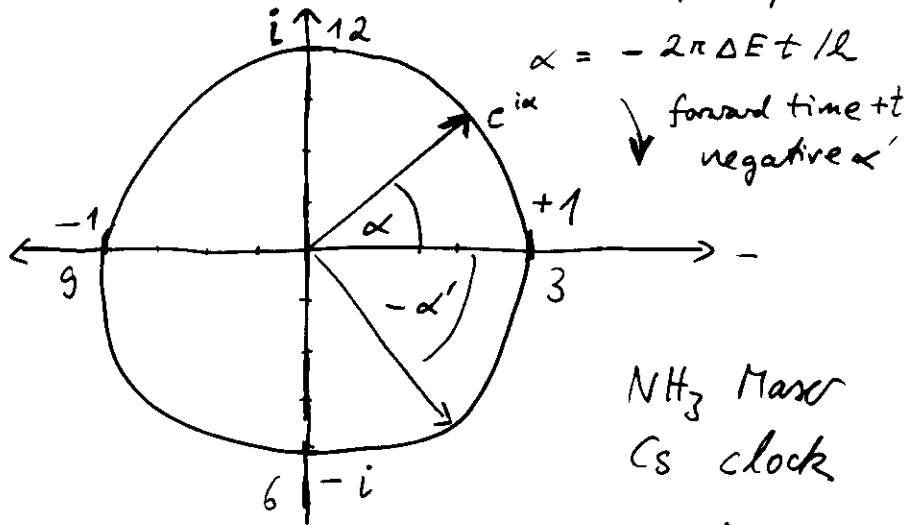
P.Q.-20-

11.2-21-
 Time dependent wavefunction
 ("de-facto" symmetry breaking)

$$\Psi(q, t) = \frac{1}{\sqrt{2}} \left\{ \chi_+(q) e^{-2\pi i E_+ t / h} + \chi_-(q) e^{-2\pi i E_- t / h} \right\}$$

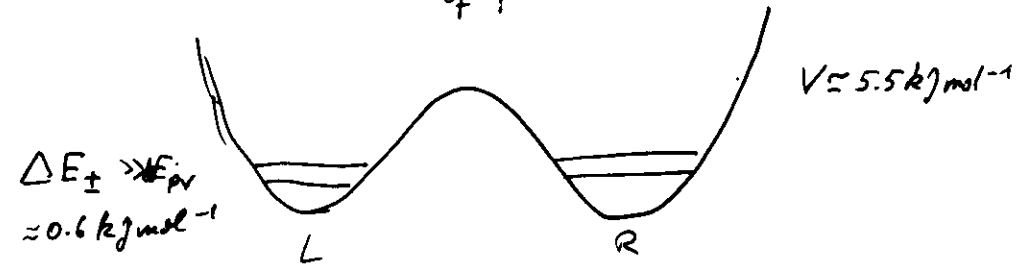
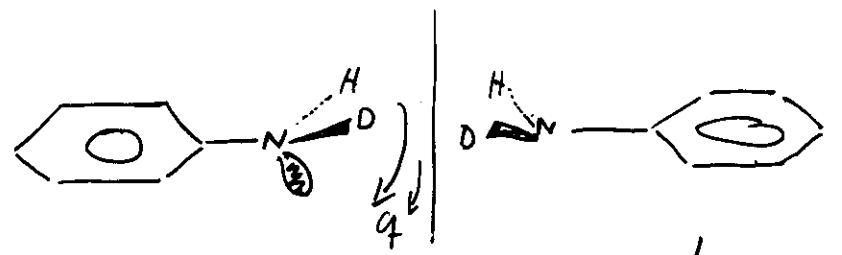
$$= \frac{1}{\sqrt{2}} e^{-2\pi i E_+ t / h} \left\{ \chi_+(q) + \chi_-(q) e^{-2\pi i \Delta E_+ t / h} \right\}$$

Atomic clock in the complex plane



Complex phase factor $\Delta \pm_{\lambda \rightarrow \rho} = \frac{h}{2\Delta E_{\pm}}$
 Period $\tau = \frac{h}{\Delta E_{\pm}}$ Hund: Chiral Molecule
 Billions of years!

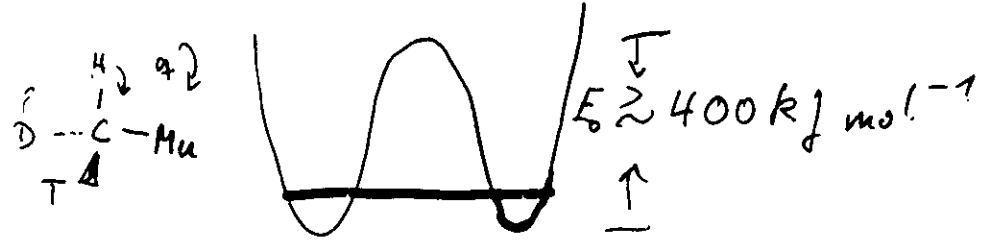
Structure and Dynamics
 Inversion made easy



$t_{\lambda \rightarrow \rho} \approx 300 \text{ fs} \ll 1 \text{ ps}$

M. Q. + Stockburger J. Mol. Spectr. 43, 87 (1972)

Inversion made hard Methane

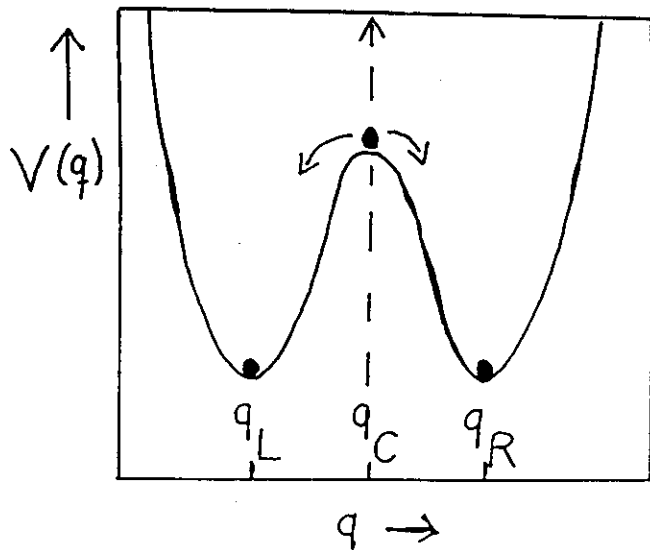


Schleyer, Knauff, Pepper, Janoschek + Quack

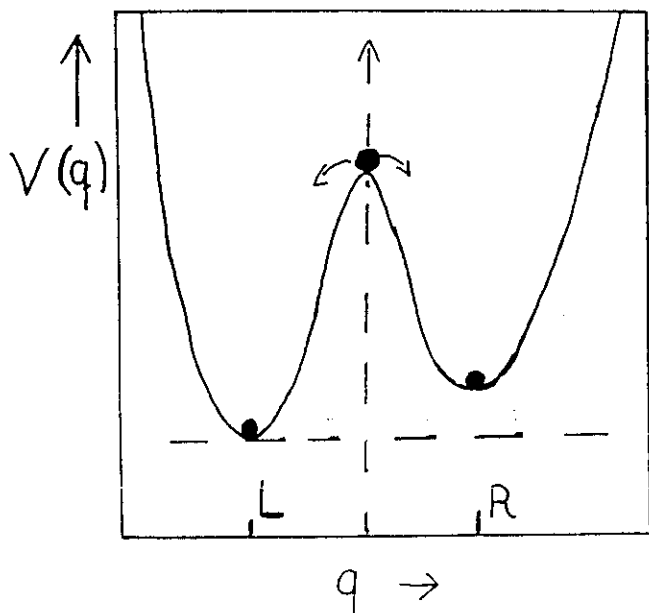
Aspartic acid $E_0 \approx 140 \text{ kJ mol}^{-1}$

Symmetry breaking

N.Q-23-



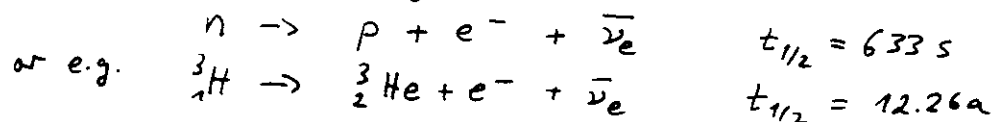
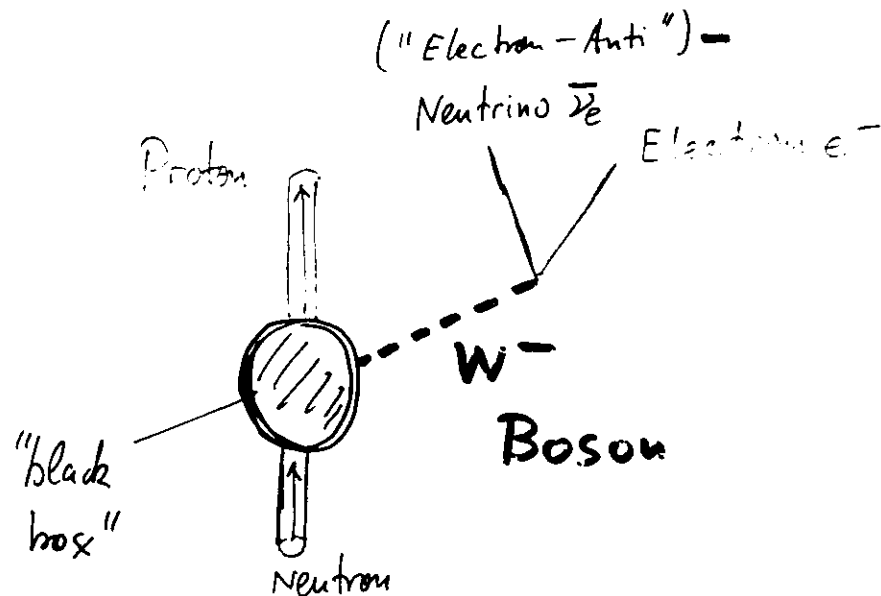
de facto



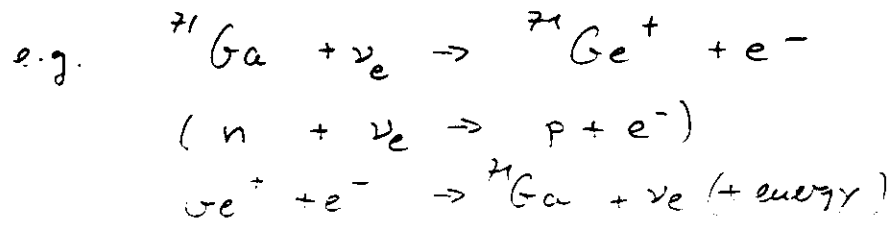
de lege

ΔE_{pv}
 } very small
 $10^{-14} \text{ J md}^{-1}$
 $\approx 10^{-13} \text{ eV}$

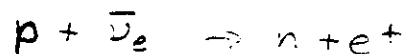
Most common occurrence
 in every day physical
 chemistry: β -decay



Measurements of Neutrinos



Similar



N.Q-24-

De lege left-right asymmetry in Physics

Most prominent examples

Neutrino (ν_e) is only left handed "chiral"



Projection of spin ($\frac{1}{2}$) $s = \frac{1}{2}$

on direction of propagation

("Helicity") $m_s = -\frac{1}{2}$ only

Antineutrino ($\bar{\nu}_e$) is only right handed

Note: For electrons we have

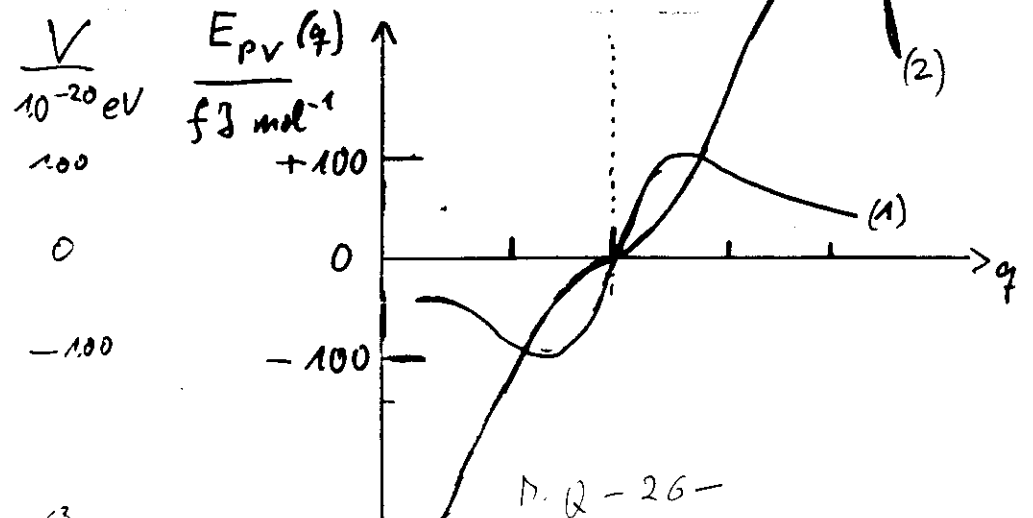
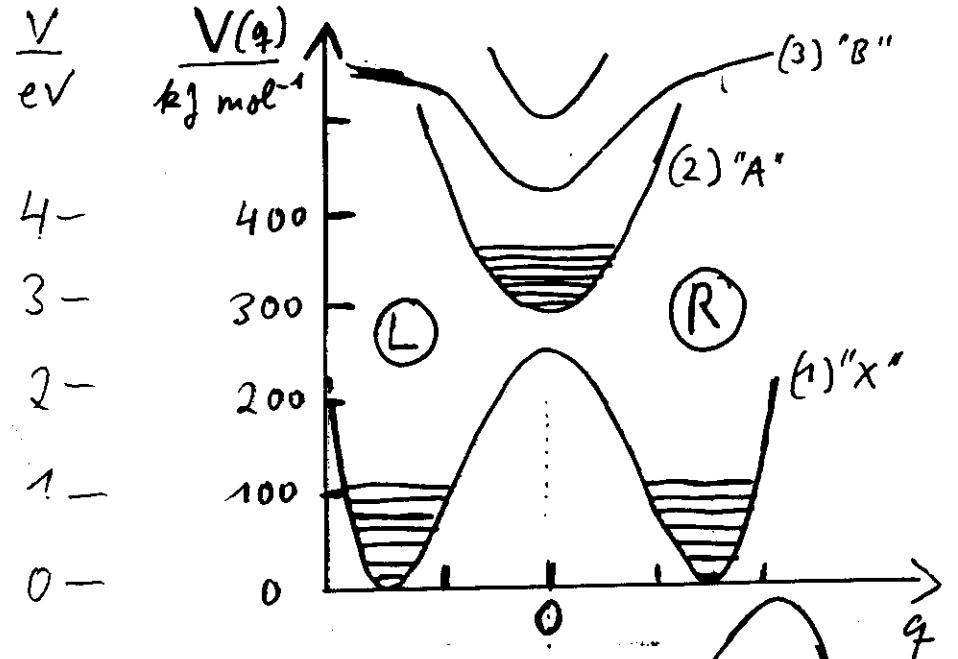
$$s = \frac{1}{2} \quad \text{and} \quad m_s = +\frac{1}{2}$$

$$\text{and} \quad m_s = -\frac{1}{2}$$

N.Q - 25 -

Electronic potential $V(q)$ and Parity violating potential $E_{PV}(q)$ in chiral molecules

$$1 \text{ fJ} = 10^{-15} \text{ J}$$



N.Q - 26 -

Some calculated ΔE_{PV}^{max}
 $\Delta E_{PV} / \text{J mol}^{-1}$ Authors/Comments

Alanine $\sim 10^{-13}$ Mason + Trauter
 L more stable

Ribose $\sim 2 \times 10^{-14}$ Trauter
 D more stable

H₂O₂ $\sim 9 \times 10^{-14}$ Mason + Trauter
 Hartree Fock (6-31G)

H₂O₂ 1.6×10^{-13} Bakasov, Ha, Quack
 Hartree Fock (TZ)
 1.7×10^{-12} CIS (D95**)

Mason and Trauter- Hartree Fock approach
 based on theory of Hegstrom, Klein, Sanders
 years 1983-1993 (1986)

Bakasov et al: recent work
 (CIS developments)

Can $\Delta E_{PV} \approx 10^{-38} \text{ J mol}^{-1} \approx 10^{-38} \text{ J}$
 $\Delta \tilde{\nu} \approx 10^{-15} \text{ cm}^{-1}, \Delta \nu \approx 10^{-5} \text{ Hz}$
 $= 10 \mu \text{ Hz}$

be of any importance for molecular
 structure and dynamics?

1. Stationary States: $\tilde{\nu} \approx 10^{10} \text{ a} \Rightarrow \nu \rightarrow \infty$

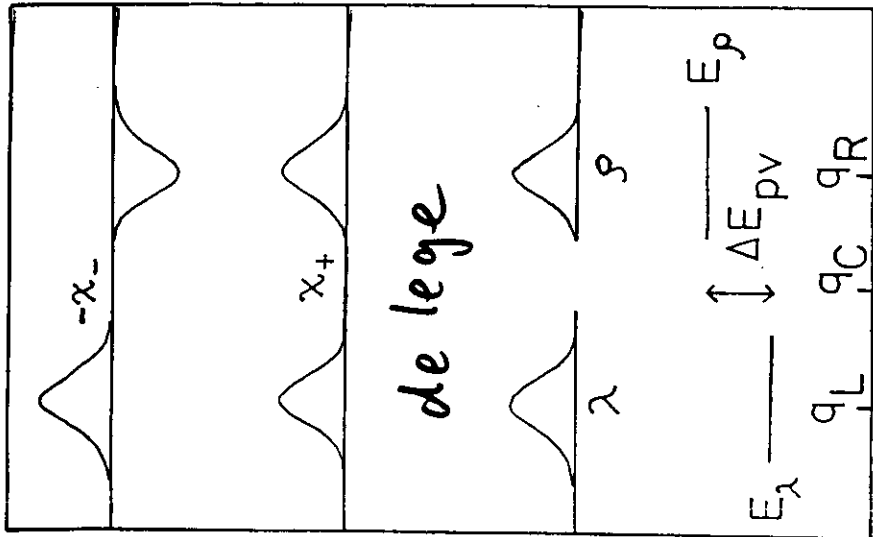
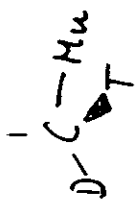
2. States of pure (+) parity $\nu = \infty$
 \Rightarrow Time dependent \sim days!

3. Kinetics of Racemization in
 the tunneling regime

4. Biological systems?
 Prebiotic selection? Biotic function?

5. Transmission of information
 about absolute Right-Left
 Structures

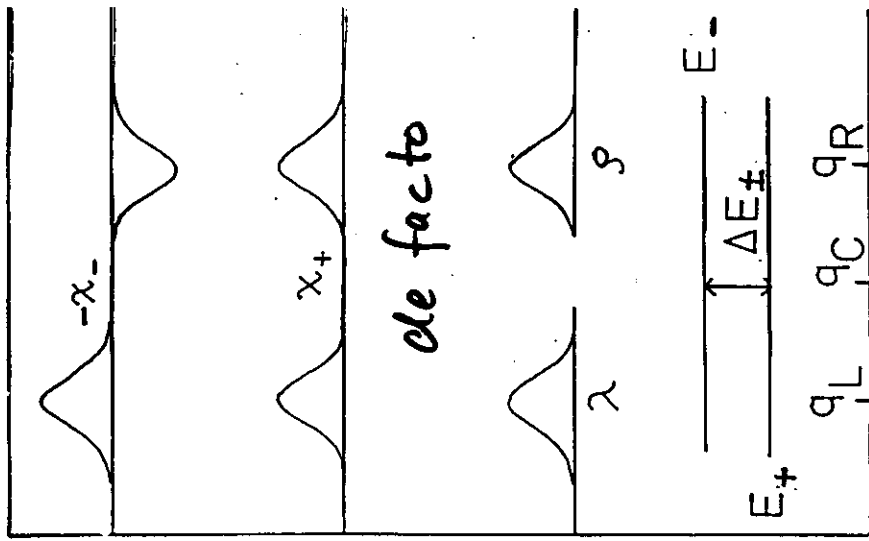
Note: Gravitation - Small cause big effects



E and ψ

17-29-04

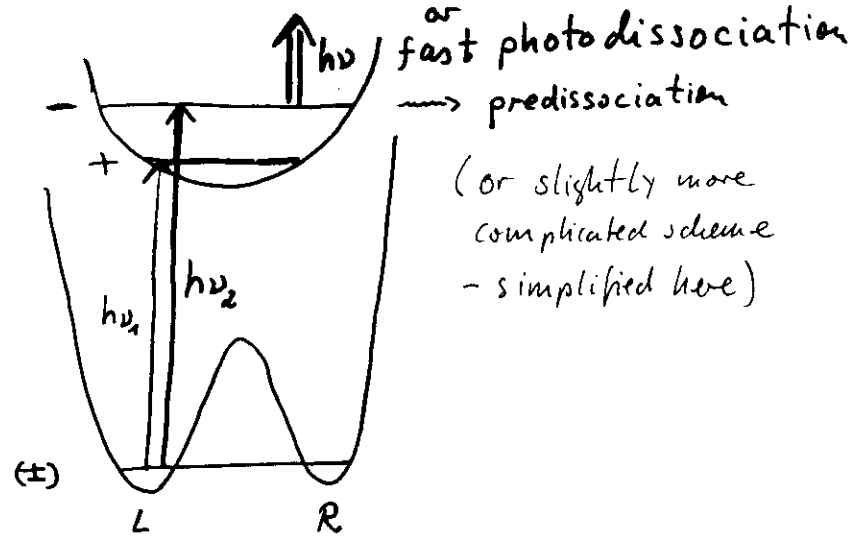
Symmetry breaking



E and ψ

Parity Selector in Surprising Experiment

17-2-30

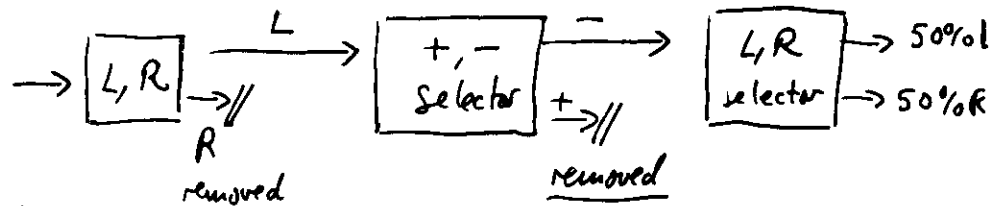


$h\nu_2$ selection of $|+\rangle$ states in ground (g) level by $|+\rangle \xrightarrow{h\nu_2} |-, \text{exc.}\rangle \rightarrow$ removal

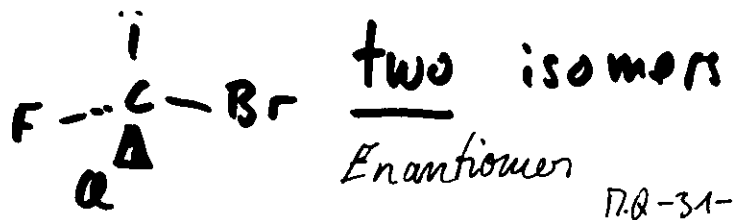
Selectivity in ground state $\approx 10^8$

Only $|-\rangle$ remain in ground state

(assuming initial jet cooling to low T)



1874



M.Q-31-

Today Four isomers by linear superposition

$$|L\rangle \quad \lambda_i = \frac{1}{\sqrt{2}} (\chi_+^i - \chi_-^i)$$

$$|R\rangle \quad \rho_i = \frac{1}{\sqrt{2}} (\chi_+^i + \chi_-^i)$$

$$|+\rangle \quad \chi_+^i = \frac{1}{\sqrt{2}} (\lambda + \rho)$$

$$|-\rangle \quad -\chi_-^i = \frac{1}{\sqrt{2}} (\lambda - \rho)$$

Note $-\chi_-$ has $P_2 = |c_2|^2 = \frac{1}{2} = |c_0|^2 = P_0$ (!)

but is not a racemate $-\chi_-$ has $p_- = 1$

racemate has $P_2 = P_0 = P_+ = P_- = \frac{1}{2}$ (!)

"L" and "R" are commonly observed

Why are "+" and "-" isomers not commonly observed?

Why are + and - isomers uncommon (not observed)?

First answer (Quack 1977/86)

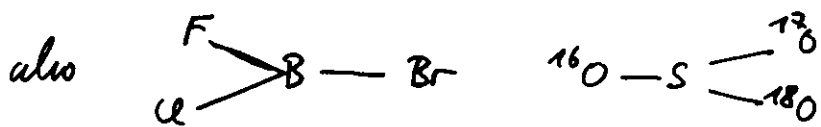
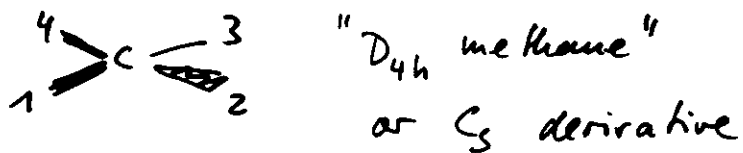
+ and - are collisionally and radiatively unstable and therefore must be prepared with special precaution (not yet done, but see analogy with free radicals, CH_3 etc., excited states, triplets etc.)

Second answer (Pfeiffer 1980, Primas 1981, Amann 1984)

They cannot be prepared because of a superselection rule, do not exist because of "spontaneous symmetry breaking" in quantum mech.

M.Q-32-

4 different atoms planar arrangement generate an achiral structure



Quantum measurement

Will (almost) always give a chiral structure, say



"Left handed" : quantum number L

"Right handed" : quantum number R

N.Q.-33-

N.Q.-34-

The result of a quantum mechanical measurement of molecular chirality is a probability distribution of

quantum numbers "L" and "R"

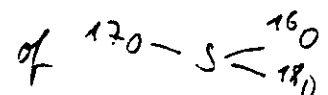
→ P(L) and P(R)

If P(L) = 1 pure chiral left handed

If P(R) = 1 pure chiral right handed

If P(R) = P(L) = $\frac{1}{2}$: achiral

(for instance the ground state

of  will come out achiral (except for weak P.V.)

Note: true for pure quantum states

General Superposition

$$\Psi = \frac{1}{\sqrt{2}} (\lambda + e^{i\alpha} \rho)$$

is always achiral: $P(L) = P(R) = \frac{1}{2}$

λ : chiral $P(L) = 1$

ρ : chiral $P(R) = 1$

Degree of chirality

$$D_K = P(K) - P(J) \quad \left. \vphantom{D_K} \right\} \begin{matrix} K, J \\ R \text{ or } L \end{matrix}$$

Absolute degree of chirality

$$D_{abs} = |P(R) - P(L)| \quad (\text{Quack 1987/99})$$

cf enantiomeric purity or enantiomer excess (ee)

$$e = \frac{x(E^L) - x(E^D)}{x(E^L) + x(E^D)}$$

(Mislow 1967 e.g.)

Summary Symmetry of Space 17.0-36-

1. The left-right mirror symmetry is broken in polyatomic molecules certainly de facto
2. The de lege violation is theoretically predicted (due to weak nuclear force) to be important if $\Delta E_{pv} \gtrsim \Delta E_{\pm}$
3. Measurement is possible via evolution of quantum number "parity" with time
4. Estimate of time scale for parity violation in molecules
 $|+\rangle \xrightarrow{\tau} |-\rangle$

$$\tau \approx \text{hours to days}$$

N.Q.-37-

5. Because of parity violation we can communicate our "absolute structure" in space: We are made of the "more stable stuff" (e.g. L-alanine)

(Provided it is matter and time runs forward)...

De lege R-L Asymmetry ^{N.Q.-38-}

Universal, Time scale ≈ 1 day

Experiment Possible but not yet existent

De lege Time a symmetry?

1. In principle, yes! CP-viol/T
CPT Schwinger-Lüder-Pauli
2. No quantitative predictions exist for molecular systems
3. No measurement

Is the second law due to symmetry breaking

De lege or De facto?

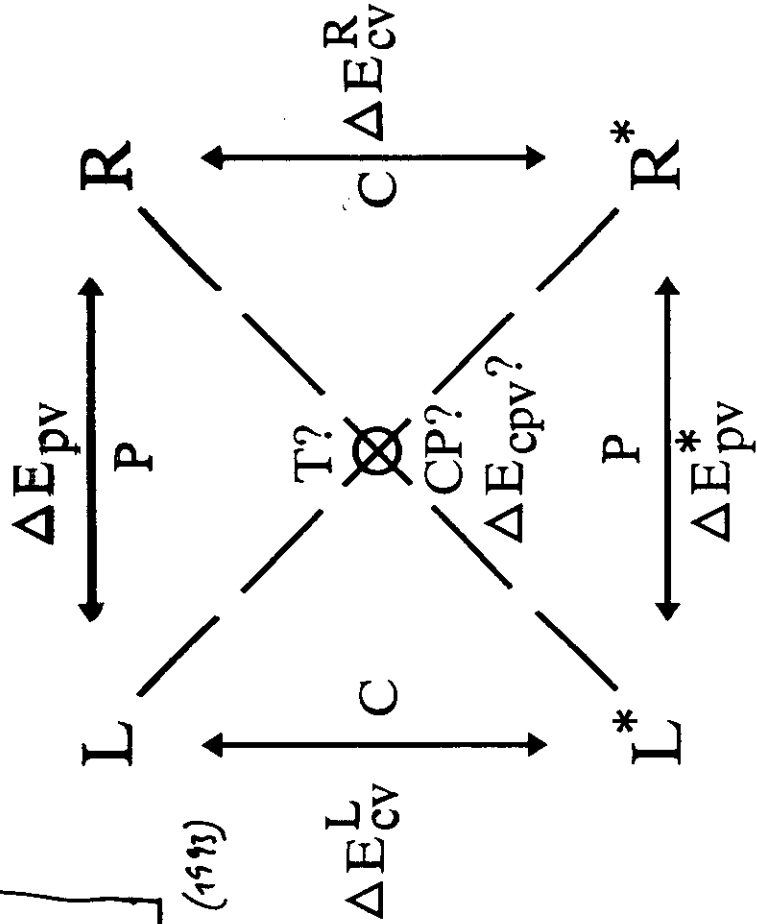
M.O. J. Mol. Struct. 292, 171 (1993)

Most sensitive test
of CPT theorem
 $\frac{\Delta m}{m} \approx 10^{-30}$

M.O. Verh. DPG VI (1993)

Chem. Phys. Lett.
(Dec. 1994)

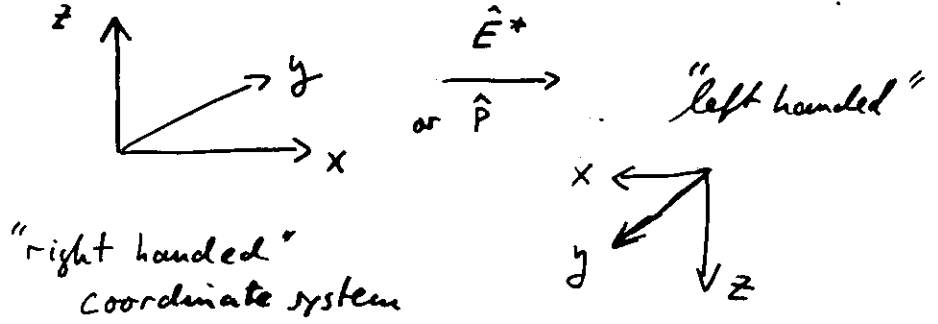
Scheme: M.O.
Bielefeld 1980



M.O. - 39 -

The symmetry of Space and Time

Space inversion



Symmetry operation

$$\begin{aligned} x &\rightarrow -x \\ y &\rightarrow -y \\ z &\rightarrow -z \end{aligned}$$

(This is a symmetry of cartesian space)

Time reversal

$$"t" \xrightarrow{\hat{T}} "-t"$$

$$\text{or } \vec{p} \xrightarrow{\hat{T}} -\vec{p}$$

This is a symmetry of ordinary mechanical (and quantum mechanical) laws.

Note x, y, z, ct in relativity
... x_1, x_2, x_3, x_4 "four coordinates" connected

Accuracy of Proposed Experiment with Chiral molecules

$$\sim 10^{-14} \text{ J mol}^{-1} \approx \Delta E (L-D)$$

$$\frac{\Delta E}{E} \approx \frac{\Delta m}{m} \approx \frac{10^{-14} \text{ J mol}^{-1}}{10^{16} \text{ J mol}^{-1}} \approx 10^{-30}$$

$\frac{\Delta m}{m} \approx$ Relative mass difference of
Enantiomers

or (with CP)

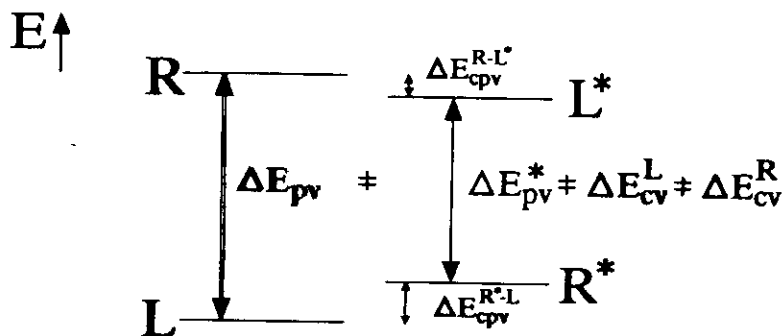
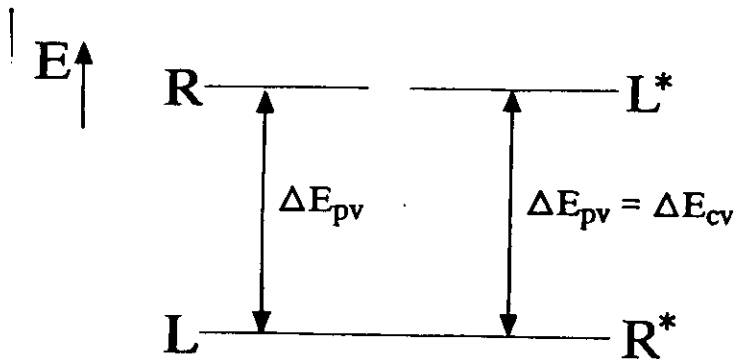
Mass difference between
Molecule "L" and Antimolecule "R"

in $CHXYZ$ and related

M. Q. J. Mol. Struct. 1993

Tests on CPT

M.Q-42-



M.Q. Chem. Phys. Lett. 1994



M.Q-41-

Current tests on CPT

High energy physics

Proton - Antiproton

$$\frac{\Delta m}{m} \lesssim$$

$$4 \times 10^{-8} \quad \text{Gabrielse improved 1995 by factor 40}$$

$\hookrightarrow 10^{-9}$ Phys Today May '95

(Gabrielse et al, CERN collab. Verh. DPG VI 1993)

Best result on baryonic matter

K^0 meson - \bar{K}^0 "mesonic best result"

$$\frac{\Delta m}{m} \lesssim 5 \times 10^{-18} \quad \text{Carosi et al 1990 CERN collab.}$$

$$\frac{\Delta m}{m} \approx 10^{-18} \quad \text{Proposed Antihydrogen CERN}$$

Hypothetical Chiral Molecule Experiment

$$\frac{\Delta m}{m} \lesssim 10^{-30}$$

(N.R. Verh. DPG VI 1993)

Chem. Phys. Lett. 231, 421 (1994)

N.R. 43-

Meeting Points "CPT"

Cosmology: $\frac{n_{\text{photon}}}{n_{\text{Baryon}}} \sim 10^9$

\hookrightarrow Baryon Asymmetry "C" $\frac{1+10^{-9}}{1} \approx \frac{\text{Matter}}{\text{Antimatter}}$

High Energy Physics

Parity Violation "P"

CP Violation in decay of K^0 Meson

(electric dipole moment of neutron??)

Atomic Physics

β -decay

optical activity of atoms

Chemistry

D-L Asymmetry?

Biological Evolution

D-L Selection

Fossils

L-amino acids

Matter

Time and irreversibility

(Pauli Principle and Particle Identity?)

N.R. 44-

The arrow of time - studied
in single, isolated molecules

Methods

1. High resolution spectroscopy

$$\text{Spectrum} \rightarrow \hat{H} \rightarrow \hat{U} = \exp(-i\hat{H}t/\hbar)$$

Dynamical loss of molecular "structure"
irreversibility and chaos

2. Time resolved kinetics and
control

M.Q-45-

Statistical Mechanics of Isolated Molecules

$\dot{Q}(t)$: Relaxation

$$\langle Q(t) \rangle_{\Delta t, t \rightarrow \infty} \simeq \langle Q(E) \rangle_{\Delta E}$$

Boltzmann-Clausius-Pauli
Entropy

$$S_f = -k \sum_j p_j \ln p_j$$

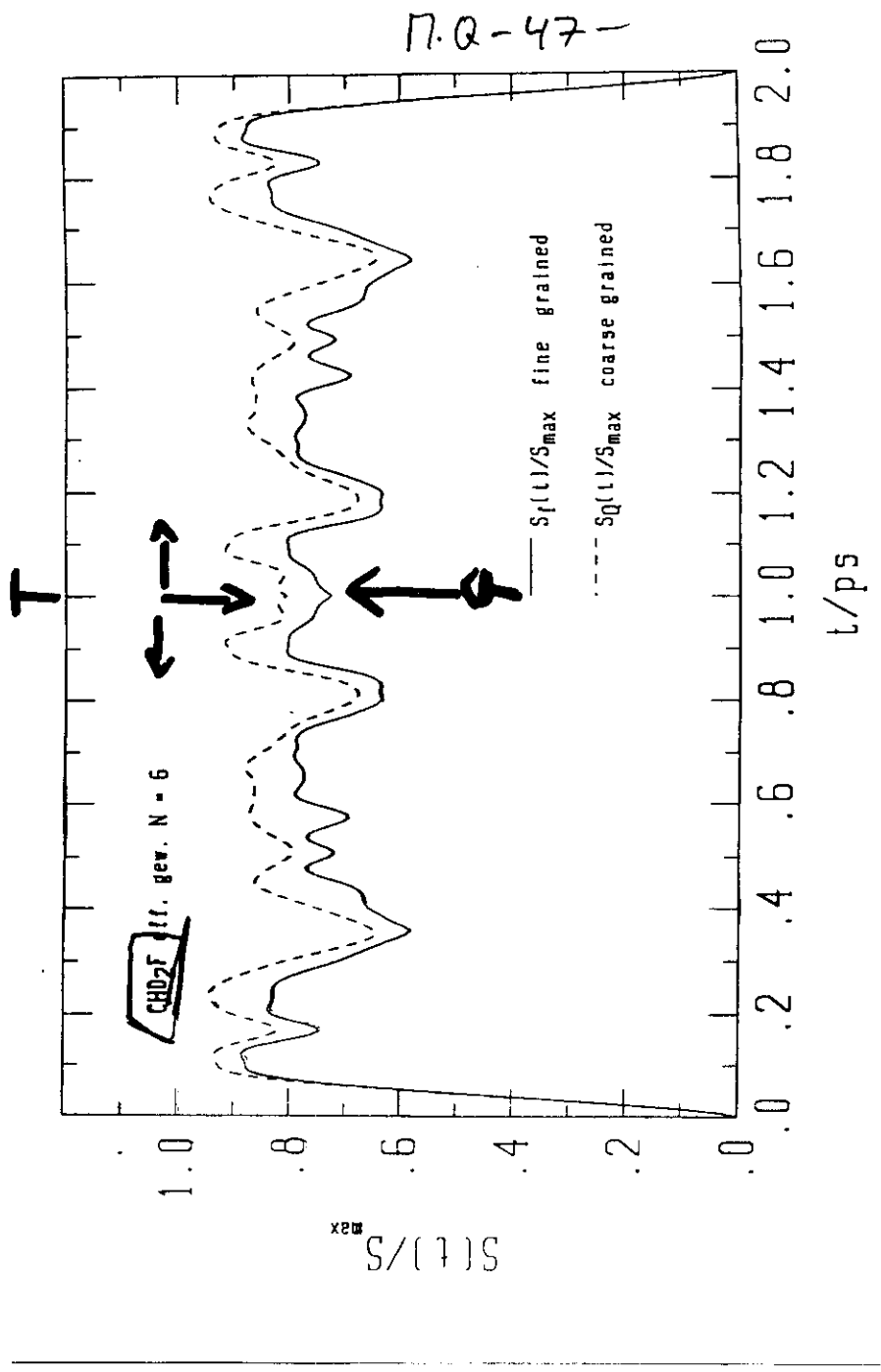
$$S_Q = -k \sum_j \langle p_j \rangle \ln \langle p_j \rangle$$

$$\dot{S}(t) \geq 0 + \text{fluctuations}$$

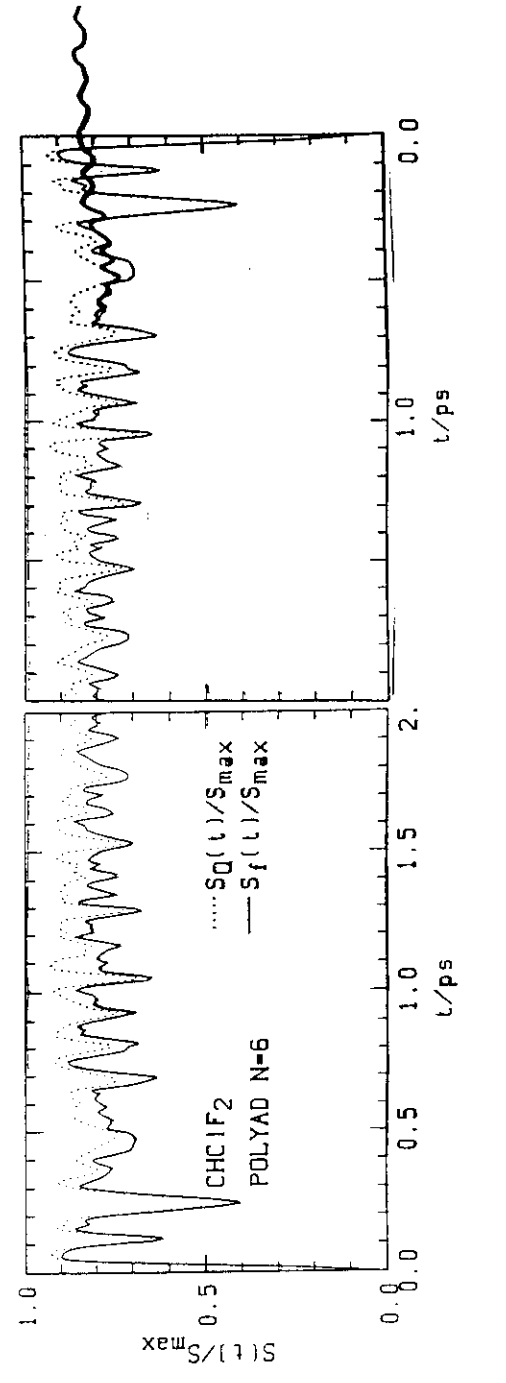
$$S_{t \rightarrow \infty} = S_{\max} + \text{fluctuations}$$

$$S_{\max} = k \cdot \ln W$$

M.Q-46-



Luckhaus, Cleary, Stolener Chem. Phys. Lett. (1983)



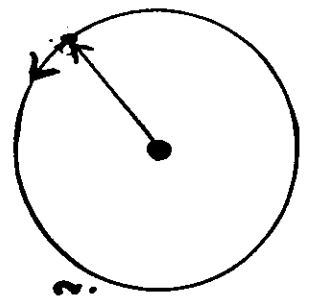
Time reversal and second law
for isolated molecules

Time asymmetry? Second law
beyond Boltzmann + Clausius

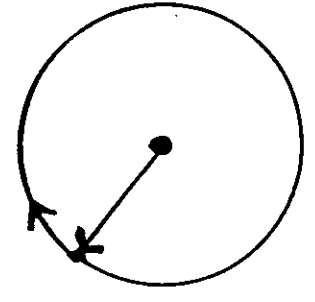
N.Q-49-

P: β -decay
 atomic optical activity Cs, Bi
 transfer of parity?
CP: K^0 Meson decay

ψ^*



ψ



T: $L - t$
 $|u_{fi}|^2 \neq |u_{if}|^2 - t$
 ?

$R + t$

Fig 6 P. Cluach J. Mol. Str. 292, 171 (1971) 347, 245 G

N.Q-50-
 Fundamental Symmetry Principles
 and Molecular Chirality
 Summary from yesterday

1. Quantum Molecular Chirality Today
 R, S, P, M Isomers
 (or $D, L, +, -$)
 chiral achiral of well defined parity
2. De facto and de lege symmetry breaking (as opposed to spontaneous)
3. Parity violation and parity violating potentials as de lege symmetry breaking in chiral molecules
 $\Delta E_{PV} \gg \Delta E_{\pm}$
4. Time reversal symmetry and symmetry breaking de facto + de lege
 CPT and chiral molecules
 → some more printed material today + tomorrow

Outlook for today

N.Q-51-

A. Beil, D. Luckhaus, R. Marquardt, J. Pochert + M.Q.

Spectroscopy of Chiral Molecules
at high and ultrahigh resolution

1. Proposed ultrahigh resolution experiment
on parity violation in chiral molecules
(energy $\Delta E_{PV} \approx 10^{-14} \text{ J mol}^{-1} \sim 10^{-19} \text{ eV}$)
2. Ultrahigh time resolution experiment
proposed for fs stereomutation control
3. Real spectroscopy at high resolution
on intramolecular energy flow
in polyatomic molecules viewed
as successive symmetry breakings
(\rightarrow chiral molecules and biomolecules)

A. Bakasov, T.K. Ha, M. Quack

Ab initio calculations of ΔE_{PV}

Why ?

N.Q-52-

Chiral Molecules in
Physical Chemistry.

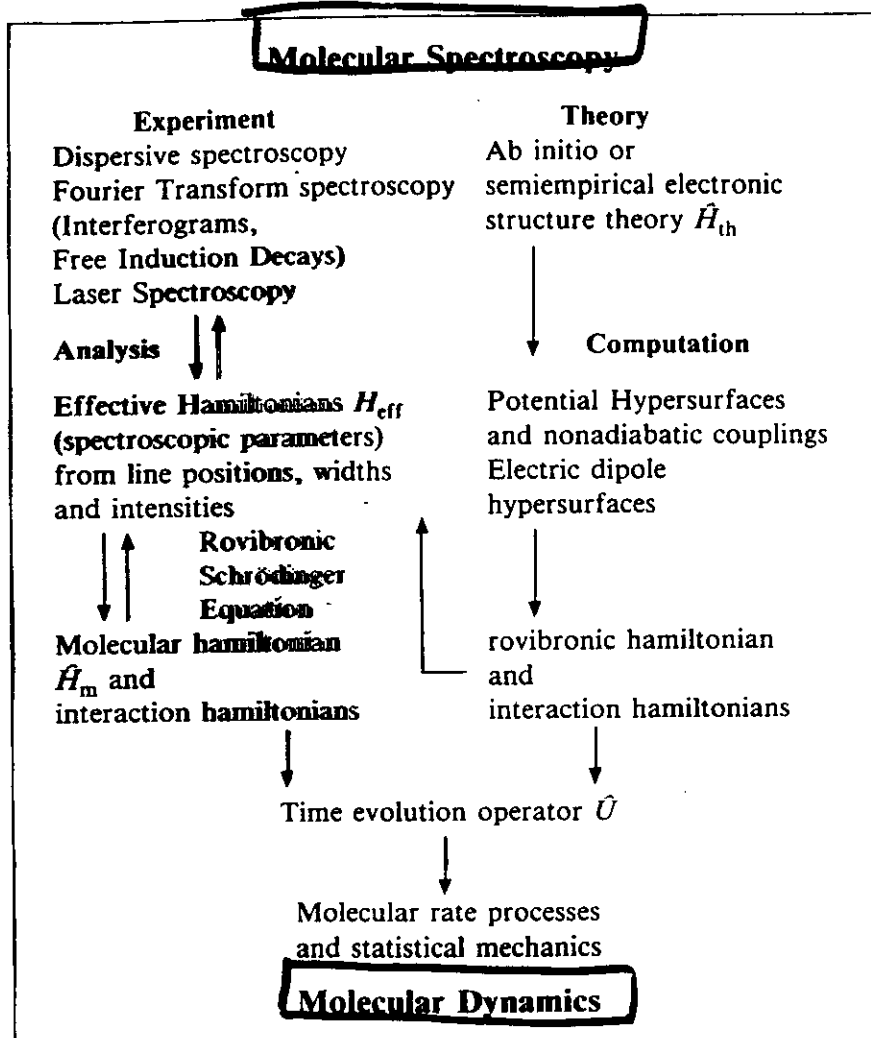
They lead to some of
the most fundamental
questions about the
structure of matter
in chemistry, physics
and cosmology !

What is new ?

Where ?

Up to date reviews (N.Q.)

1. Special issue of Berichte der Bunsenges. Physik. Chem. March 1995
99, 231 N.Q. + W. Kutheilig
2. Femtosecond chemistry eds. Manz / Woeste eds. Verlag Chemie 95
27 chapters (chapter 27 by N.Q.)
(in 2 volumes) (↳ fundamentals)
3. Infrared Laser Chemistry
Infrared Phys. Technol. 36, 365 (1995)
4. Molecular Infrared Spectra and Motion
J. Mol. Struct. (Encmos 22 issue)
(1995) 347, 245
5. Ann. Rev. Phys. Chem. 41, 833
1990



Scheme 1

N.Q.-53-

lar structure and dynamics including adequate, careful formulations of the underlying molecular hamiltonian [1-4, 161-166]. This procedure has been understood to fail for

**Current experimental techniques in Zürich group
(IR Spectroscopy)**

1. FTIR bandwidth 0.004 cm^{-1} since 1981 (Prototype BOMEM)
10 to 16000 cm^{-1} including long path (100 m) gas cells
2. FTIR Supersonic Jet absorption
at 0.004 cm^{-1} (apodized) $\approx \Delta\tilde{\nu}$
Developed 1984-1994, see Ann. Rev. Phys. Chem. 41, 839 (1990)
3. Diode laser supersonic jet absorption
(pulsed slit nozzle) $\Delta\tilde{\nu} \approx 0.001 \text{ cm}^{-1}$ ($800-3000 \text{ cm}^{-1}$)
(Hollenstein, Quack, Richard, Chem. Phys. Lett. 1994)
4. **Overtone Spectroscopy by Vibrationally Assisted
Dissociation and Multiphoton Ionization ("OSVADPI")**
Hippler + Quack, 1994 development
 $\Delta\tilde{\nu} \approx 0.02 \text{ cm}^{-1}$ ($8000-16000 \text{ cm}^{-1}$) + ISO3
J. Chem. Phys. 1996
5. Kinetic diode laser spectroscopy
Uncertainty limited $\Delta t \lesssim 2 \text{ ns}$; $\Delta\tilde{\nu} \lesssim 30 \text{ MHz}$
He, Quack, Ranz, Seyfang CPL 1993 NIR
Cros, He, Quack, Schmid, Seyfang CPL 1993 MIR
Faraday Discussion 102 (1995/96)

CHBrClF, slitjet, Res. 0.001 cm^{-1}

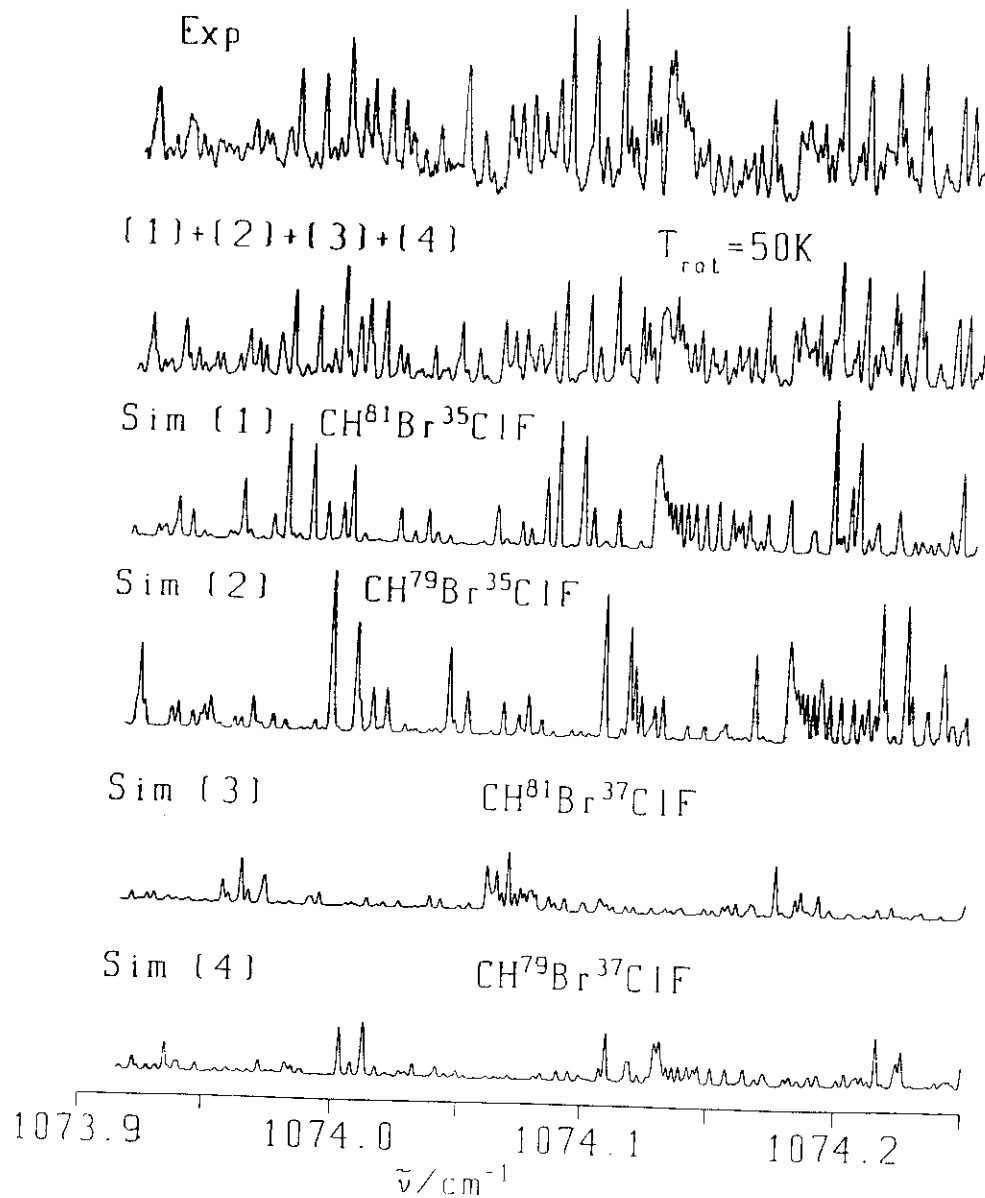
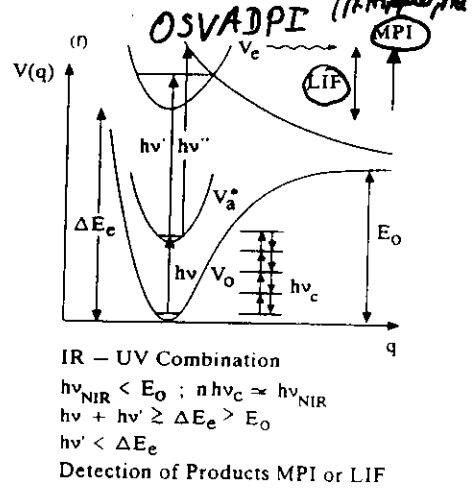
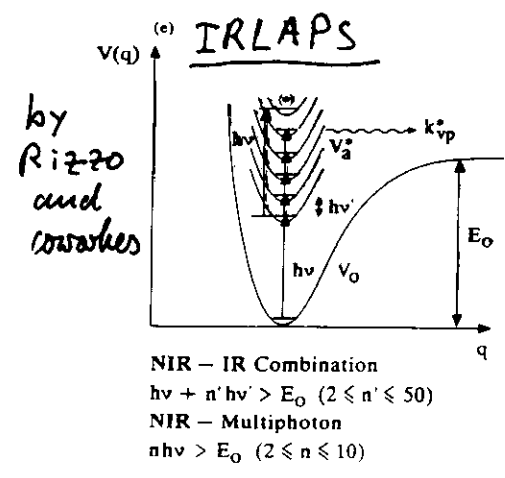
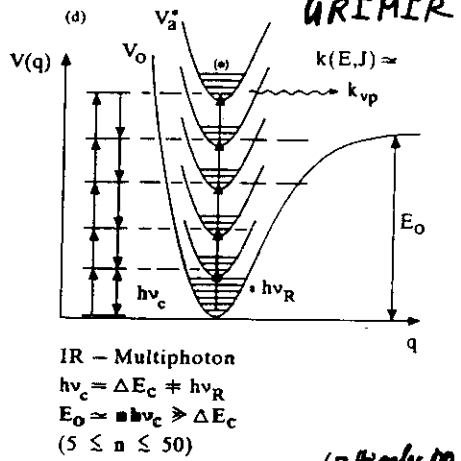
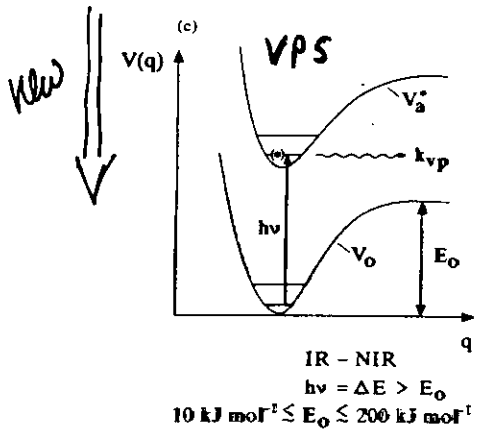
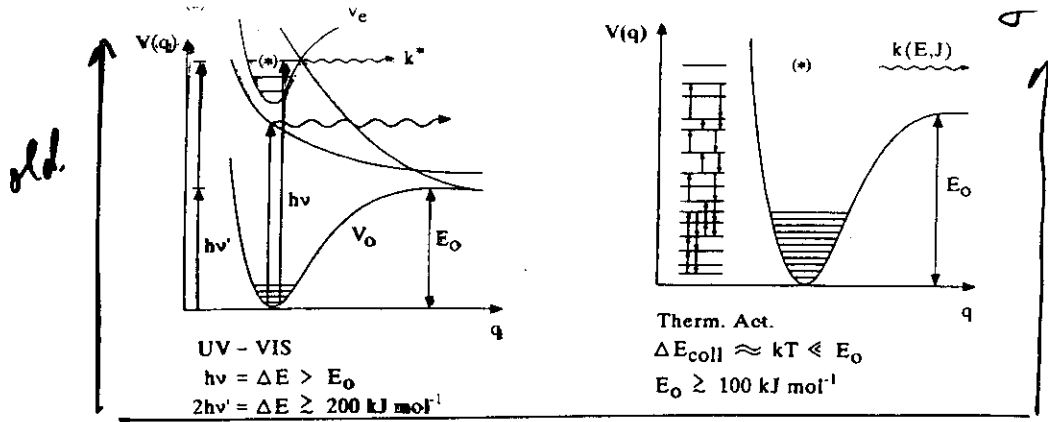


Fig 3 Beil, Luckhaus, Margardt, Quack



Control of symmetry of initial state

↓

time dependence of the symmetry properties?

↓

Test of fundamental symmetries in nature (such as P, T, CP, CPT)

or

Test of approximate symmetries of the dynamics

Scheme: Control of symmetries in dynamics

M.Q. 57-

Fig. 1. Survey of the schemes for ordinary thermal chemistry and photochemistry as related to various schemes for infrared laser chemistry (see detailed discussions and explanations in the text).

M.Q. - 56-

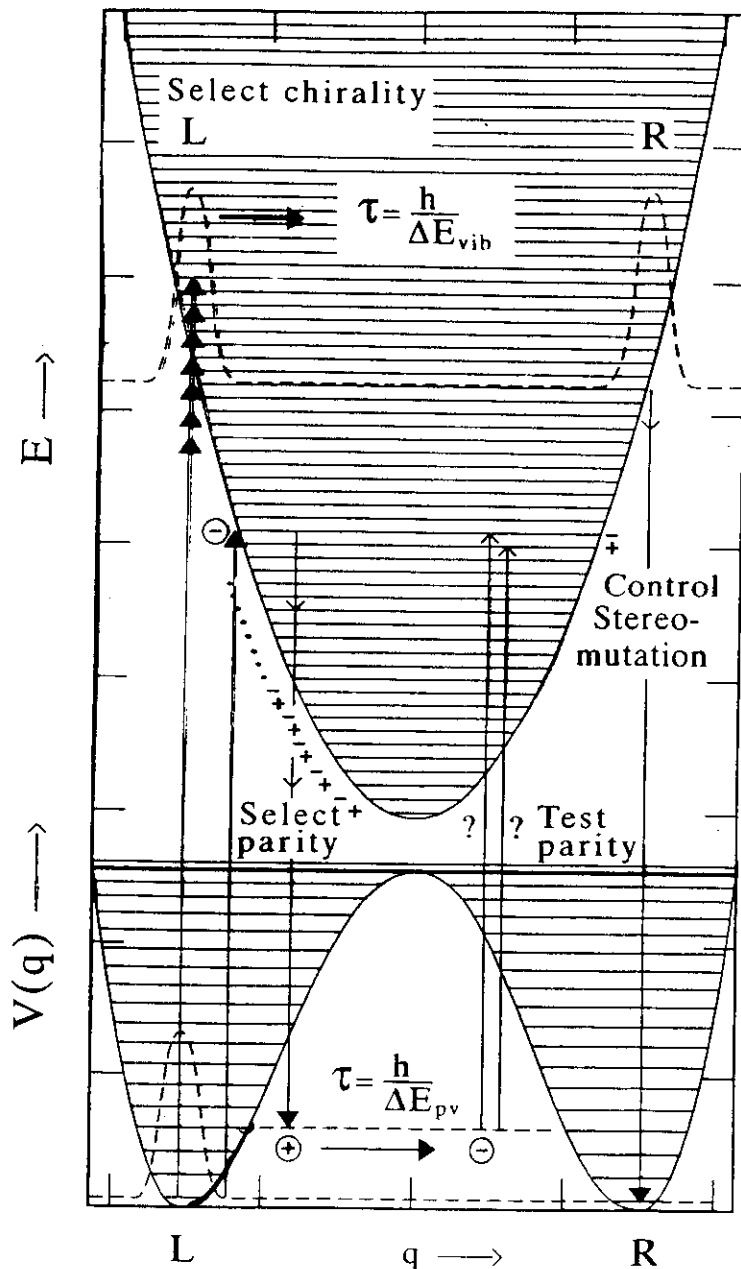


Fig. 2 (HD-Disk.020) 12.1

ON THE MEASUREMENT OF THE PARITY VIOLATING ENERGY DIFFERENCE BETWEEN ENANTIOMERS *

Martin QUACK

Laboratorium für Physikalische Chemie, ETH Zürich (Zentrum), CH-8092 Zürich, Switzerland

Received 22 August 1986

An experiment is outlined for measuring the small energy difference between two enantiomers due to the parity-violating weak neutral current perturbation. The method is based on the violation of the selection rules for the time evolution of states of well defined initial parity in isolated molecules. It could confirm or reject recent quantitative theoretical estimates of parity-violating energy differences.

1. Introduction

Since the early investigations of Pasteur [1] and van 't Hoff [2], molecular chirality has been of interest to chemists, with many important advances even in the last decades [3,4]. The spontaneous occurrence of enantiomeric substances and the prevalence of one type over the other in biology has often led to discussions touching epistemology, natural philosophy (see ref. [2, p. 100] and refs. [5,6]) and, perhaps, "molecular theology" in Prelog's phrasing [4]. The classic discussion in the framework of quantum mechanics has been given by Hund [7], according to whom the fundamental left-right symmetry is broken de facto by the isolation of very slowly varying time-dependent states.

The physical situation has changed drastically with the discovery of parity-violating interactions in elementary particle physics [8] and later in atomic spectroscopy [9,10]. These interactions break the left-right symmetry de lege. This has led to renewed interest and numerous fundamental discussions of the physics of chirality in recent years (see refs. [11-20] and the literature cited therein). An important step forward has been provided by quantitative and apparently reliable estimates of the parity-violating energy

differences between various enantiomers [21-25]. For instance, in the case of α -amino acids the calculated energy differences are of the order of 10^{-14} J mol $^{-1}$, corresponding to about 10^{-15} cm $^{-1}$ or 3×10^{-5} Hz in spectroscopic units [25].

Even if one is optimistic concerning present day quantum chemistry and the inclusion of parity-violating weak neutral current perturbations, it seems important to have some direct experimental access to such small quantities. An early attempt from Letokhov's group was published in 1976 [26]. Subsequently [27], an alternative technique was discussed which might be efficient in some molecules if the parity violating energy difference (hereafter ΔE_{pv}) is large enough; at the time this appeared to be uncertain. Because of recent careful estimates of a relatively large ΔE_{pv} [25], it seems suitable to describe the principle of the proposed experiment in more detail.

2. The principle of the experiment

The experiment consists of three steps:

- (i) Preparation of molecular states of well defined parity from optically active molecules of ill defined parity.
- (ii) Free evolution of the isolated molecule with initially well defined parity.
- (iii) Observation of the population of states of the

Presented at the ETH/Weizmann Institute Symposium and dedicated to Professor Vladimir Prelog on the occasion of his 80th birthday.

0 009-2614/86/\$ 03.50 © Elsevier Science Publishers B.V. (North-Holland Physics Publishing Division)

147

M.Q-60-

M.Q-58-

Measurement of parity violating ΔE_{pv}

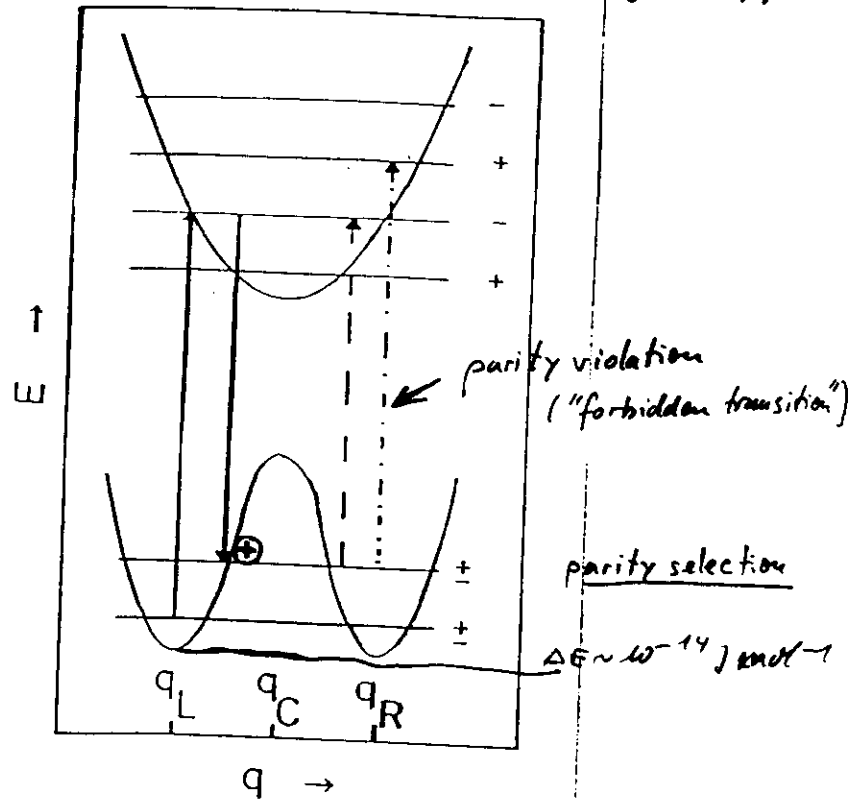
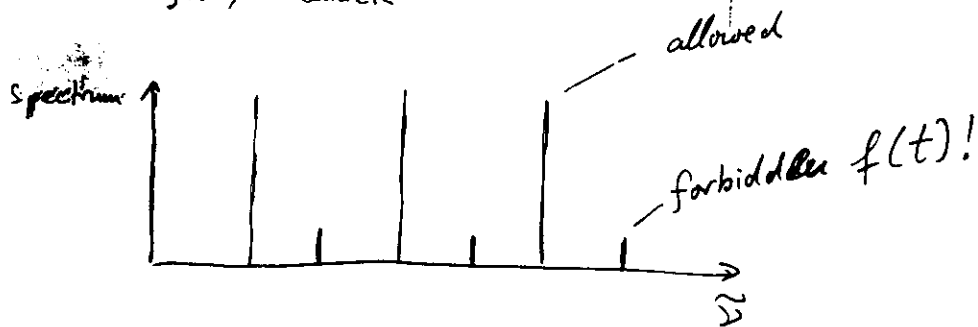


Fig 1, M. Quack



The Experiment

$$P_- = |c_-|^2 \approx (\pi \Delta E_{pv} t / \hbar)^2$$

n.q-61-

Parity is not a constant of the motion or good quantum number in chiral molecules

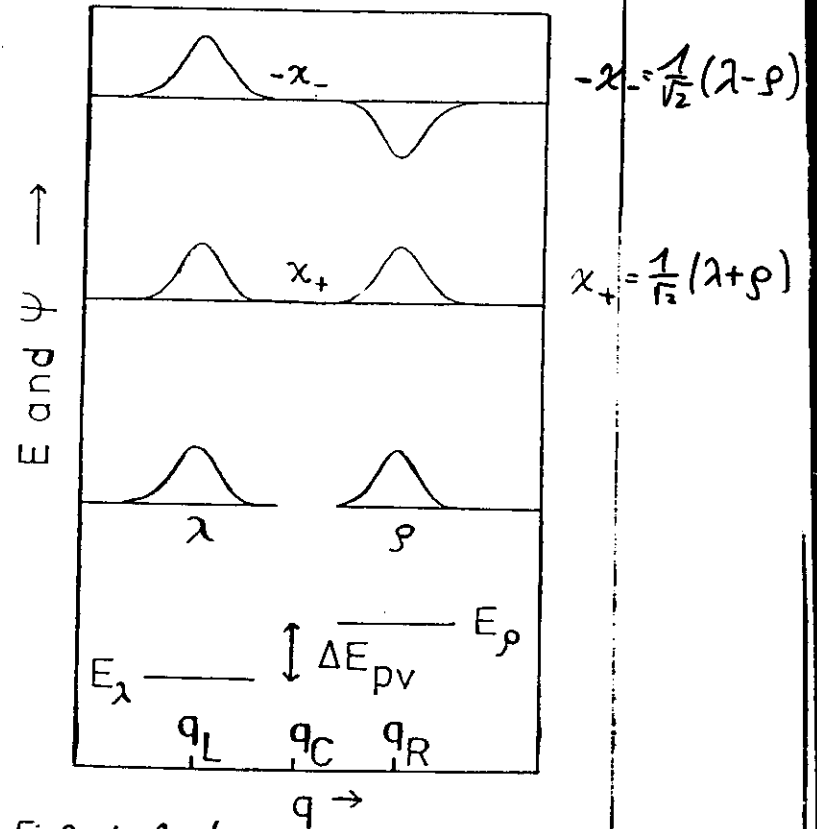


Fig 3 M. Quack

$$\psi(t) = \frac{1}{\sqrt{2}} e^{-iE_\lambda t/\hbar} (\lambda + \rho e^{-i\Delta E_{pv} t/\hbar})$$

short times

$$P_- = |c_-|^2 = (\pi \Delta E_{pv} t / \hbar)^2$$

Time evolution of Parity

Control of
Stereo mutation
and
Exponential decay
for a
Harmonic Oscillator Model

(R. Marquardt and N. Q.
Z. Phys. D. 1996
F. Hund special issue)

N.Q-63 -

Is the Stereomutation of Methane Possible?

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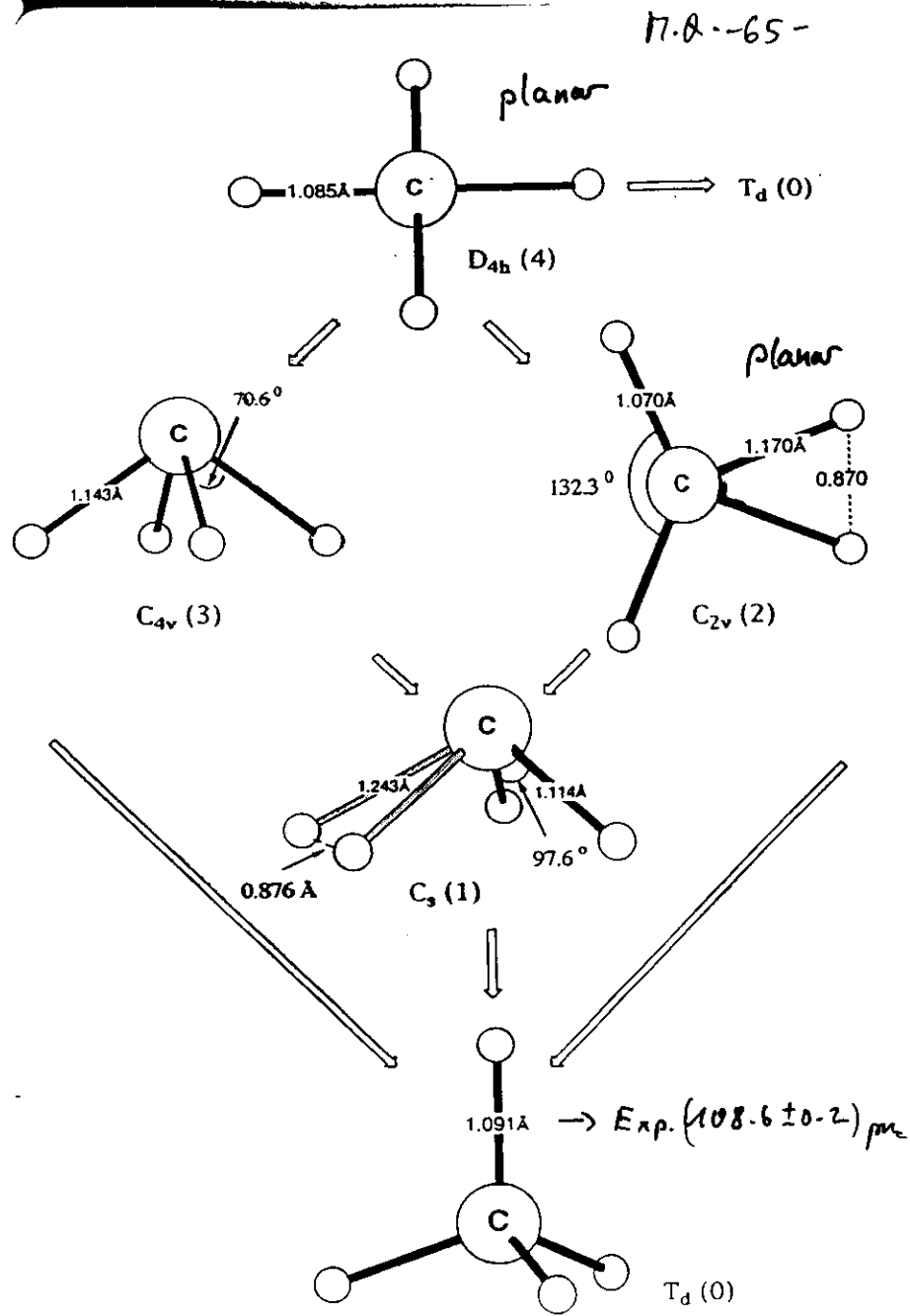
Received 6 October 1993; accepted 20 June 1994

ABSTRACT

Large basis set *ab initio* calculations at correlated levels, including MP2, single reference, as well as multireference configuration interaction, carried out on the methane potential energy surface, have located and characterized a transition structure for stereomutation (one imaginary frequency). This structure is best described as a pyramidal complex between singlet methylene and a side-on hydrogen molecule with C_{2v} symmetry. At the single reference CI level, it lies 105 kcal/mol above the methane T_g ground state but is stable relative to dissociation into $CH_2(^1A_1)$ and H_2 by 13 kcal/mol at 0 K (with harmonic zero point energy (ZPE) corrections for all structures). Dissociation of the transition state into triplet methylene and hydrogen also is endothermic (by 4 kcal/mol), but single bond rupture to give CH_2 and H is 3 kcal/mol exothermic. Thus, it does not appear likely that methane can undergo stereomutation classically beneath the dissociation limit. Confirming earlier conclusions, side-on insertion of 1A_1 CH_2 into H_2 in a perpendicular geometry occurs without activation energy. Planar (D_{3h}) methane (130.5 kcal/mol) has four imaginary frequencies. Two of these are degenerate and lead to equivalent planar C_{2v} structures with one three-center, two-electron bond and two two-electron bonds and two

*Authors to whom correspondence may be addressed.

N.Q-64 -



Scheme 1 *Popper, Schläger, Farnochek, Alcock*
Chem. Abstr. (Elektronen)

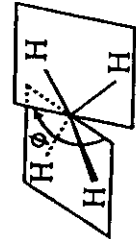
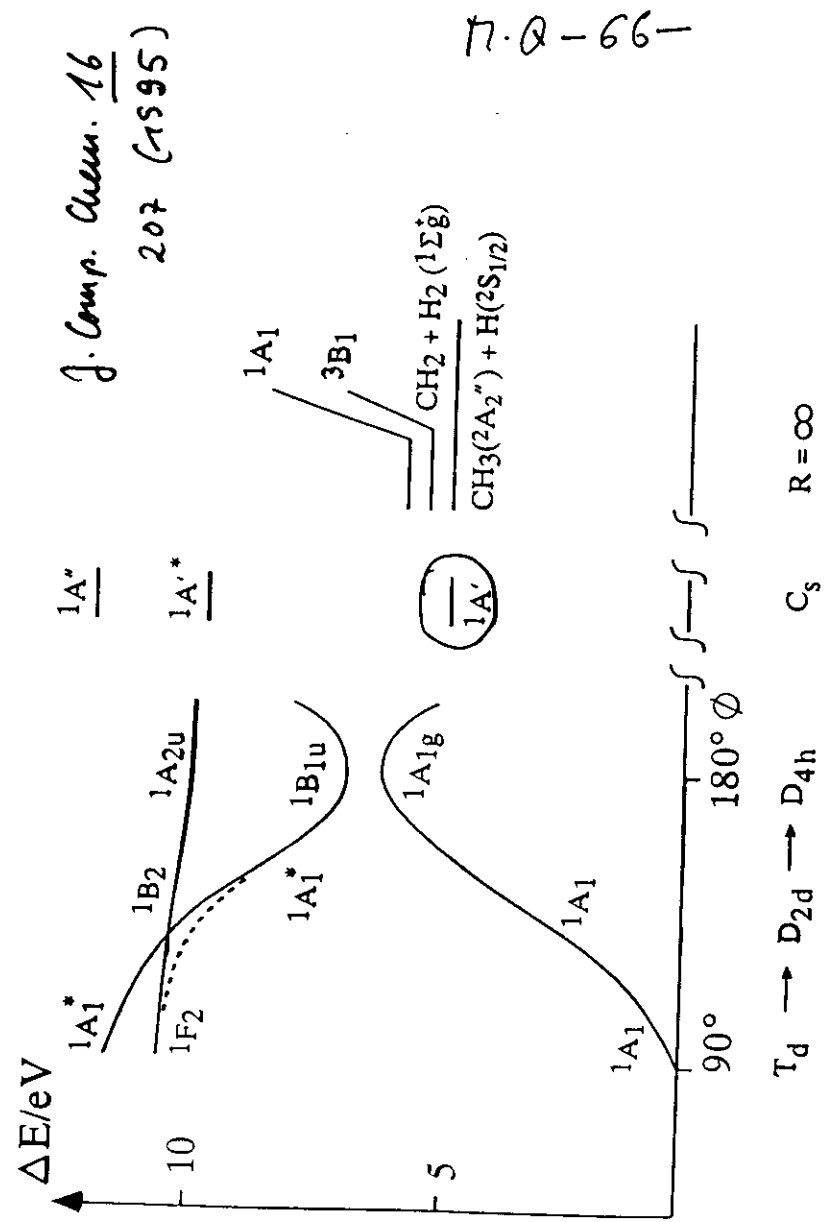


Fig. 1 *Popper, Schläger, Farnochek, Alcock*
Chem. Abstr. (Elektronen)

running microresistant
56 10120

N.Q.-67-

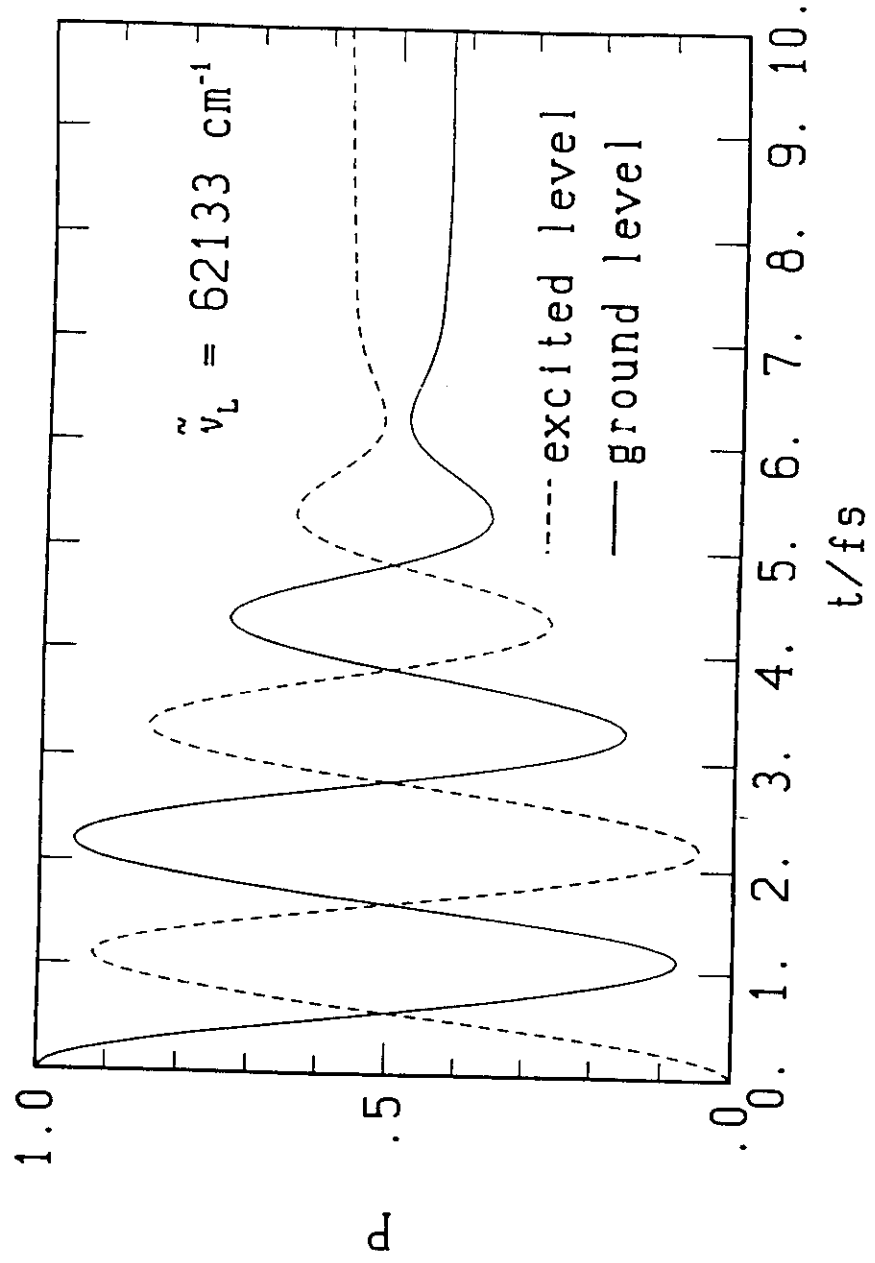
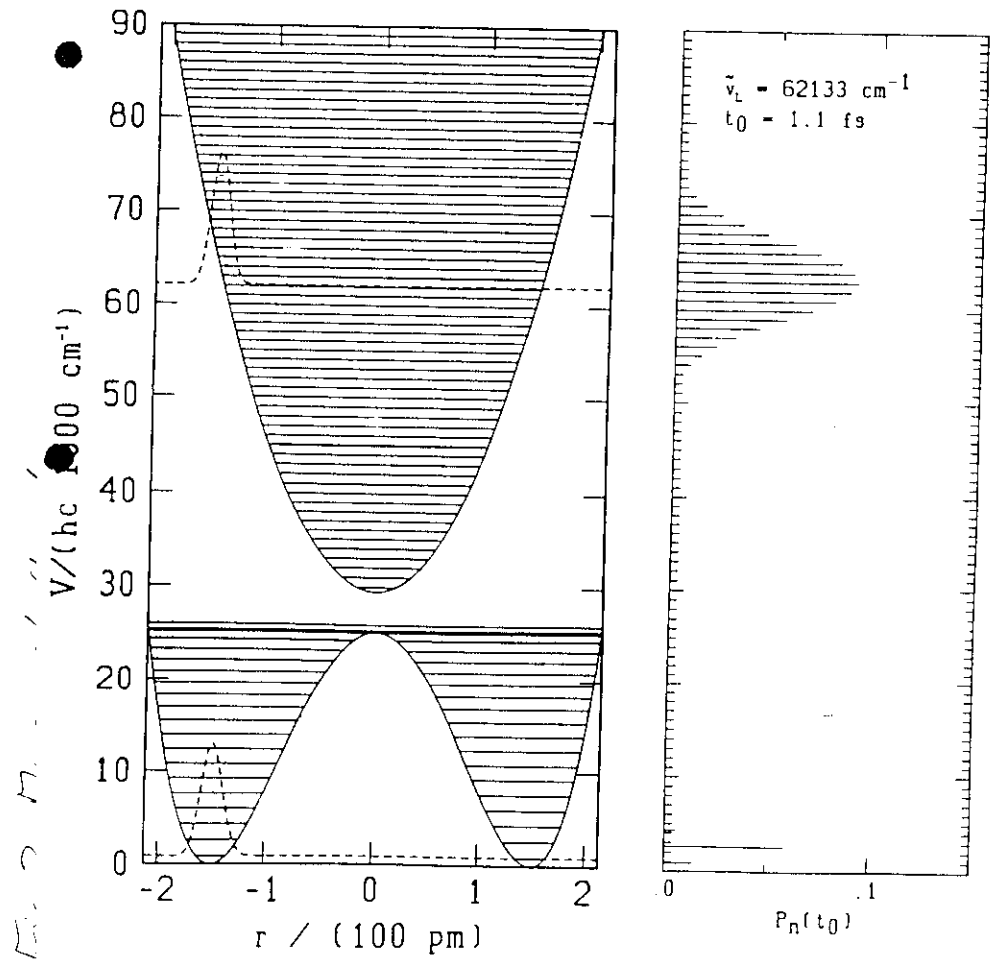


Fig 2
Marginalite Crystal
N.Q.-68-



MODEL 1: PROJECTION UPPER LEVEL (FIELD FREE)

17. Q-69-

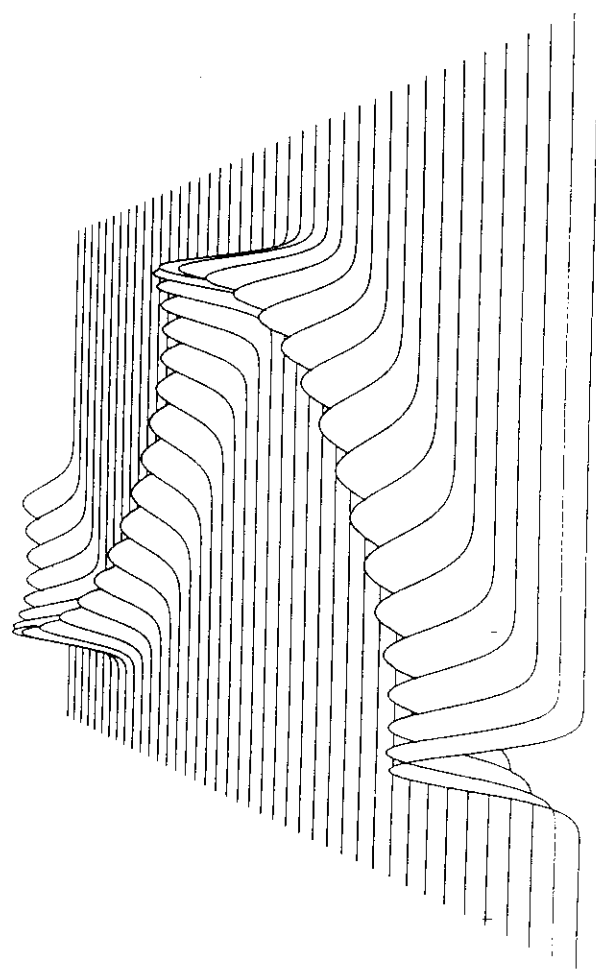


Fig 4 Purquardt Ulbrack

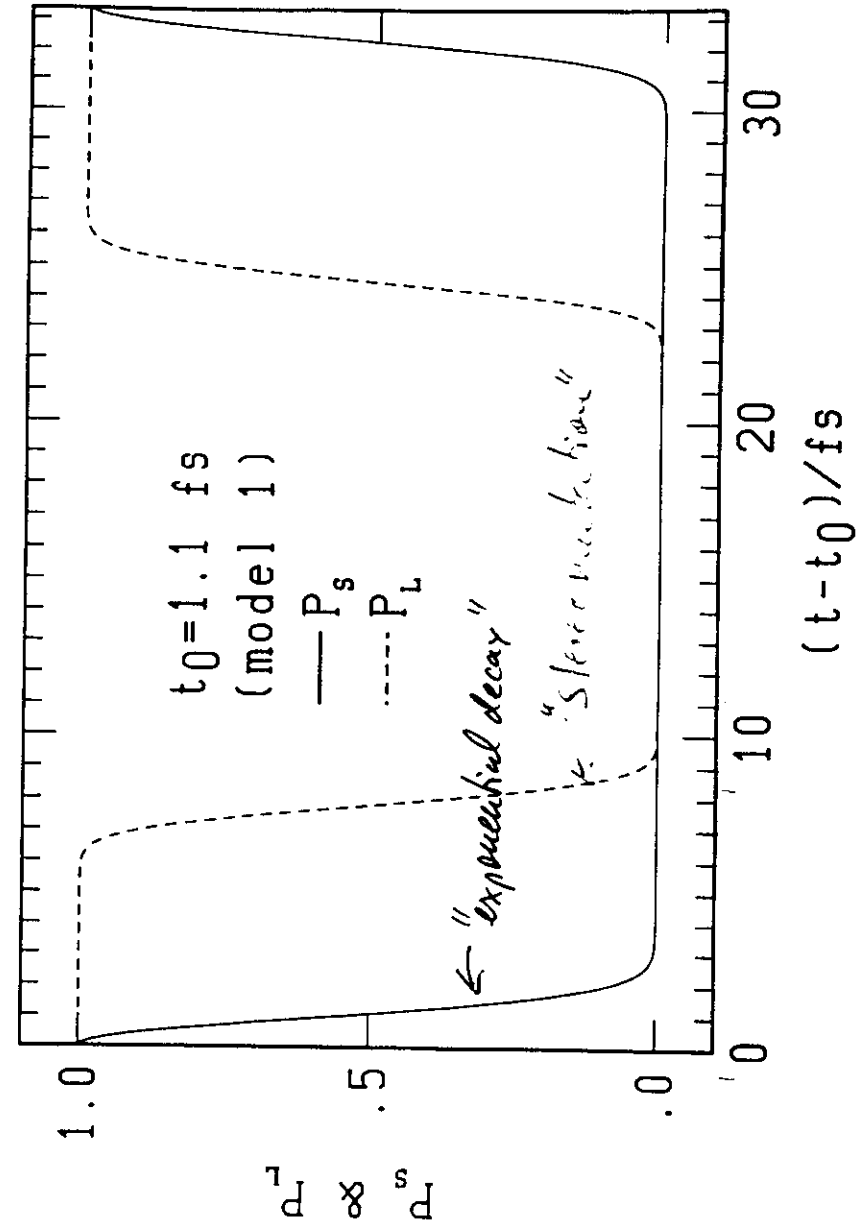
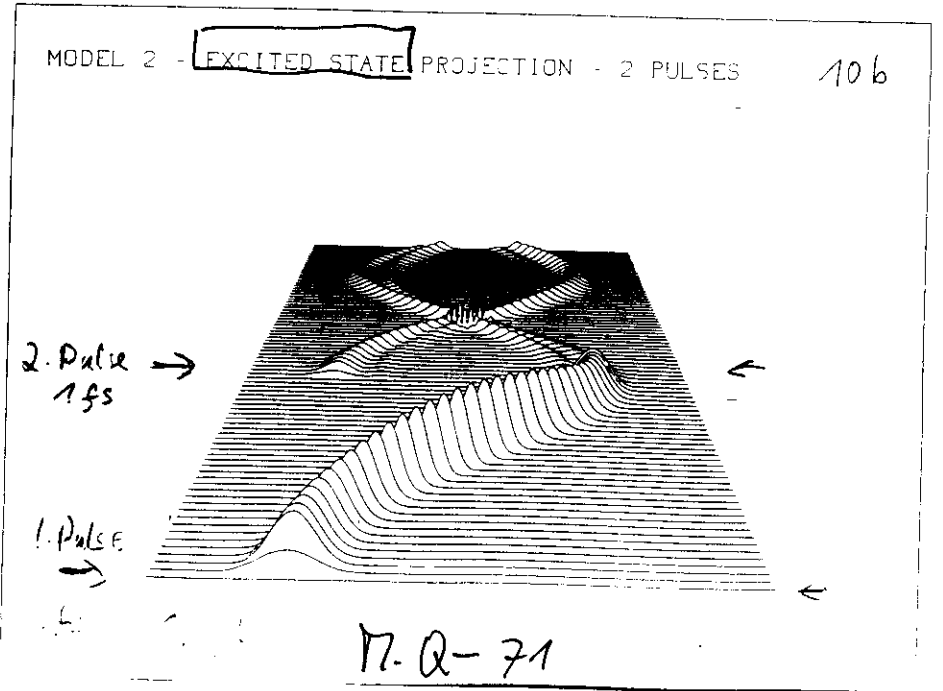
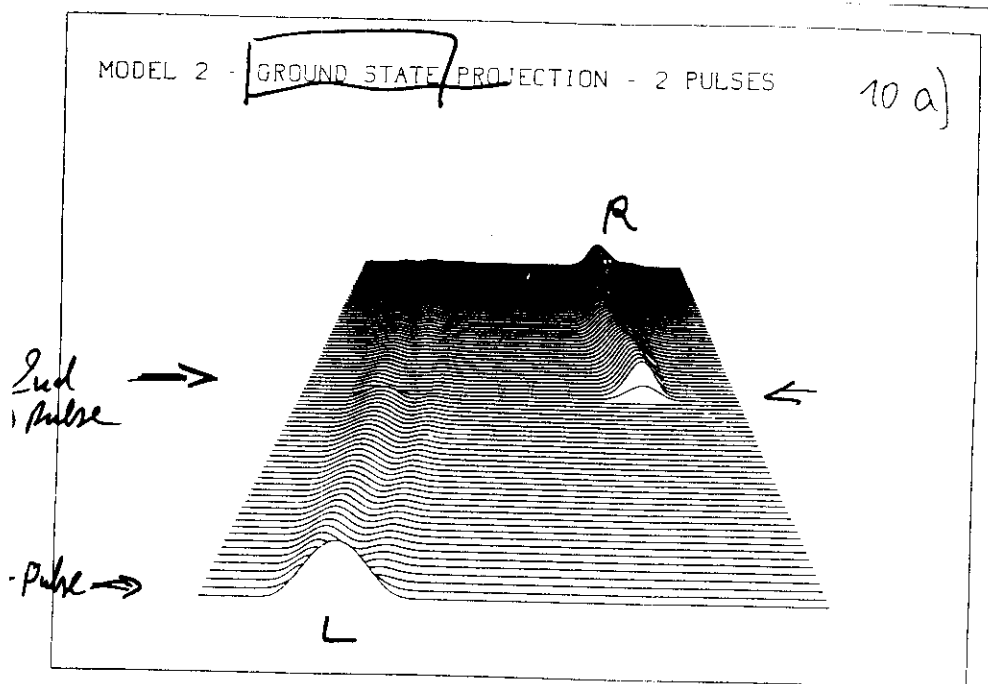


Fig 5 Purquardt Ulbrack

11. Q. - 71 -
 Summary of simple harmonic oscillator
 dynamics of stereomutation



1. Quasi Rabi-like inversion between ground and excited electronic state
2. Quasi-exponential decay of survival probability by simple wave packet translation in 1-d space!
3. Control of stereomutation by a 2-pulse sequence with fs UV pulses

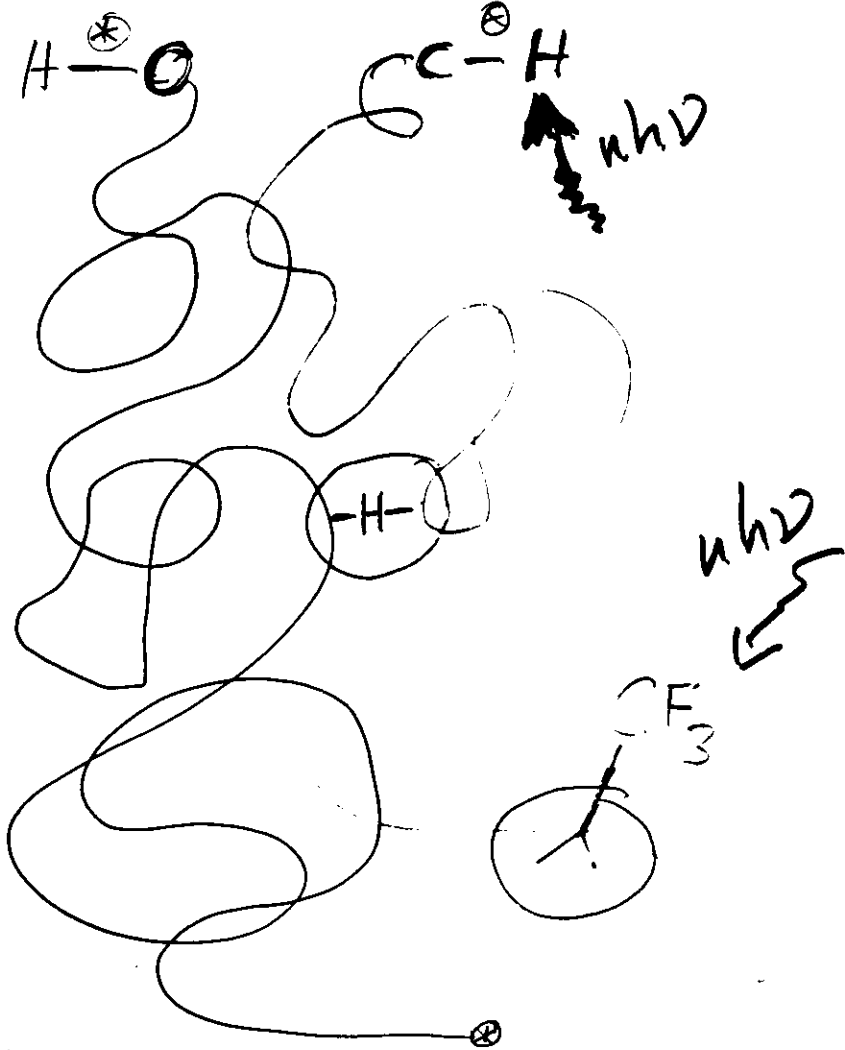
Problem UV-Vis
 Short time - high intensity → Ionization
 Long-time - low intensity → Intramolecular Relaxation

→ Much better in Infrared

Large Molecules

"Quantum Chemistry and Biochemistry"
 (Staudinger, Chargaff, Eschenmose
 Crick + Watson, Pauling, ...)

Chiral!
 why?



Collaboration by Till, Niels + Manfred Q.
 11. Q-73 -

Understanding Intramolecular Quantum Dynamics

$$\hat{H}_m \psi(x_1, x_2, \dots) = E \psi(x_1, x_2, \dots)$$

$$\Psi(x_1, x_2, \dots, t) = \hat{U}(t, t_0) \Psi(x_1, x_2, \dots, t_0)$$

$$i \frac{\hbar}{2\pi} \frac{\partial \hat{U}}{\partial t} = \hat{H} \hat{U} \quad \hat{H} = \hat{H}_m \text{ or } \hat{H}(t) = \hat{H}_m + \hat{H}_{\text{dipole coupl.}} \dots$$

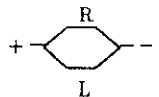
$$\hat{P}(t) = \hat{U}(t, t_0) \hat{P}(t_0) \hat{U}^\dagger(t, t_0)$$

$$\hat{Q}(t) = \hat{U}^\dagger(t, t_0) \hat{Q}(t_0) \hat{U}(t, t_0)$$

11. Q-74 -

*URIMIR Package Quack + Sutcliffe Q.C.P.E. 1986
 + extensions thereof

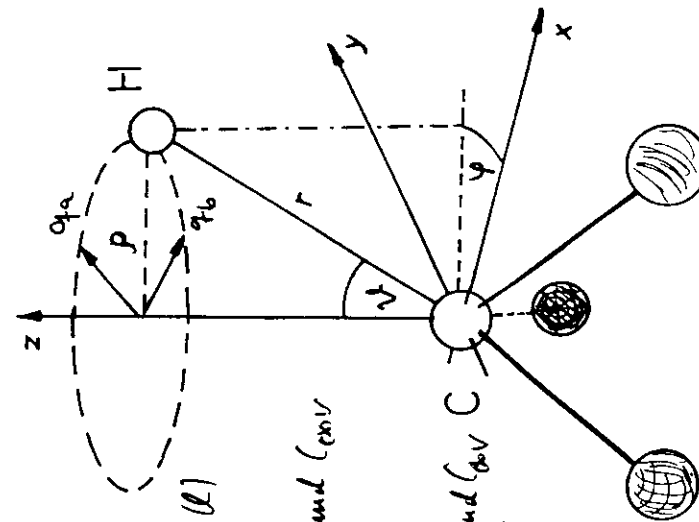
SYMMETRY REDUCTION

Example	Γ	O (Group)	Spectrum
1. R-C≡C-H	$\nu_s, \nu_b, \ell (+, -)$	(∞)	—
2. X ₃ CH (X = D, F...)	N, $\ell (+, -)$	(∞)	≡≡≡
3. X ₃ CH (—)	A ₁ [±] , A ₂ [±] , E [±] (N)	S ₃ [*] (12)	≡≡≡≡≡
4. FX ₂ CH (X = D, Cl) F ₂ XCH	A ^{i(±)} , A ^{u(±)} (N)	S ₂ [*] (4)	≡≡≡≡≡
5. FXYCH (X, Y = Cl, Br) (X, Y = ³⁵ Cl, ³⁷ Cl)	A ⁺ , A ⁻ (N)	S ₁ [*] (2)	≡≡≡≡≡ + - ? + - ? + - ? ...
6. FXYCH (as 5.)	A (N)	S ₁ (1)	

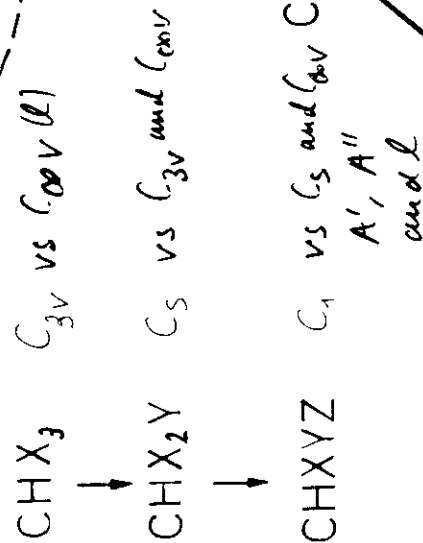
N.Q-75-

N.Q-76-

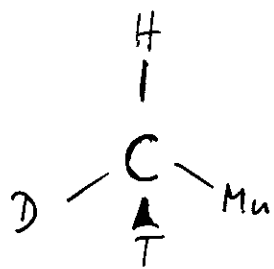
\hat{H}



Symmetrie
Reduktion

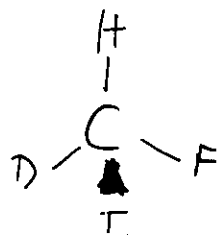


$$\hat{A} = \hat{H}_{\text{symmetrical}} + \hat{H}_{\text{asymmetry}}$$



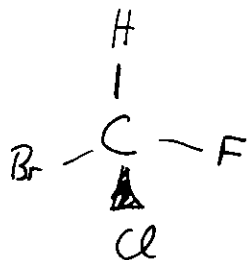
Methane
Theory

Checked by Exp.
on other isotopomers
 CHD_3 etc.



Methyl fluoride
Theory

(checked by
 CHD_2F
experiments)



Fluoro-chloro-
-bromo methane
Experiment
and Theory

Intramolecular Vibrational Redistribution
Spectroscopy
Femto second Dynamics

Fundamental Question

Symmetry Breaking and Dynamics

Possible Application

Time dependent Vibrational Optical Activity

eil, Luckhaus, Nawrodt, *Accad Faraday Disc.* 99 (1994)

N.Q-77-

Conclusions - take-home Message

1. Anharmonic coupling of normal modes corresponds to time-dependent anharmonic symmetry breaking:

quantum numbers v_s, v_a, v_b, \dots
are not conserved if (e.g.)

$t > 20 \text{ ps}$ for $sp \equiv C-H$

$t \geq 100 \text{ fs}$ for sp^3 alkyl CH

Quantum Statistical Dynamics
as opposed to Quasiclassical Motion

2. l_b - quantum number is approx.
conserved in C_{3v} (i.e. effective $C_{\infty v}$)

3. l_b not good in C_s (even if
only by isotopic substitution,
 l_b not good in C_1 either)

N.Q-78

Conclusions ---

4. A' , A'' is good in C_S
but quickly (~ 100 fs), incompletely
violated by anharmonic
 $k_{\text{stab}} \approx 25 \text{ cm}^{-1}$ in C_1 CHFClBr
(only moderately strong)

5. De-facto breaking of
time reversal symmetry is
visible in isolated molecules
("2nd law of thermodynamics")

6. Open Questions (Experiment)

Parity conservation in isolated molecules?

De-facto violation of time reversal
symmetry in molecules?

De-facto violation of CP and CPT?

17.12-79-

M. Muck
To be reprinted
with lecture notes
Trieste 96

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Reprint

Structure and Dynamics of Chiral Molecules **

By Martin Quack *

Could there be chiral methane? What is the characteristic structural feature (in a physicochemical sense) of a molecule? This question dates back to *Louis Pasteur*, the discoverer of molecular chirality, and since the work of *van 't Hoff* and *Le Bel* is generally considered by chemists as solved. In the present article it is pointed out that there exist fundamentally conflicting theoretical views of the physical origin of molecular chirality. These views predict consequences that could, in principle, be distinguished experimentally, but at present there is no conclusive experimental evidence available. Possible experiments are suggested that test different hypotheses. The importance of the magnitude of the parity-violating energy difference ΔE_{pv} in molecules due to the weak nuclear force for both the structure and spectra of chiral molecules and for the kinetics of racemization is discussed. The chemical relaxation rate coefficient of chiral molecules with some appreciable energy of excitation is derived for several limiting cases of a simple statistical mechanical model, which takes ΔE_{pv} into account.

*"Si les principes immédiats de la vie immédiate sont dissymétriques, c'est que, à leur élaboration, président des forces cosmiques dissymétriques; c'est là, suivant moi, un des liens entre la vie à la surface de la terre et le cosmos, c'est-à-dire l'ensemble des forces répandues dans l'univers". [***]*
L. Pasteur^[19]

1. Introduction

Since Pasteur's first separation of crystals of racemic organic compounds (such as the sodium ammonium salt of tartaric acid) into left- and right-handed, optically active compounds 140 years ago,^[1] two major questions related to this observation of chirality have been addressed repeatedly:

1. What is the origin of chirality in *molecular physics* and thus the "nature" or intrinsic structural feature of a chiral molecule or chiral substance?
2. What is the origin of chirality in (molecular) *biology* (i.e. the *chiral bias* favoring some enantiomers over others)?

These two questions are quite distinct, although related to each other. The second question concerns one of the more obvious, major unsolved problems in biochemical research.^[2-17] We shall concentrate here on the first question, which is considered by many to be solved. This is not so, as we shall demonstrate. It may be that proper consideration of the first question will help to solve the second.

Even today the "structure" of chiral molecules is discussed by most chemists in terms of *macroscopic molecular models* in three dimensional space in the framework of conventional

stereochemistry.^[1c,3,18-23] It was recognized by *Friedrich Hund*^[24] that in the framework of quantum mechanics certain problems arise with classical stereochemistry due to the possibility of tunneling, which connects left- and right-handed structures. *Hund* provided an immediate apparent solution to these problems by considering the time scales for interconversion between enantiomers (see Section 2.2). *Primas*^[25] pointed out, however, that this solution does not explain, why one cannot buy in a drug store the substance corresponding to the coherent superposition of left- and right-handed states of chiral molecules such as alanine. Of course the reason for this may be trivial, the superposition states may be unstable and thus difficult to store in bottles (one cannot buy free radicals such as CH_3 in bottles in a drug store, but there is good evidence for their existence). However, a *possible* solution of "Primas' paradox" is the nonexistence of these achiral states of chiral molecules, which leads to the more recent discussions of chirality.^[26-32] These invoke either essential interactions with the radiation field, or else with other external agents in order to explain the physics of chiral molecules.

Finally, after the discovery of the chiral symmetry violating weak nuclear interaction^[33-41] it would appear natural to assume that this force has also fundamental implications for the physics of chiral molecules.^[10,11,17,42-54] In contrast to the other three fundamental forces of physics (strong nuclear forces, electromagnetic interaction, and gravitation) this "weak interaction" is intrinsically chiral. It is responsible for the β -decay of the neutron. It has been shown to lead to a nonconservation of the quantum number "parity" in nuclear decay processes^[34] and in atomic spectroscopy.^[40] In chemistry it has a most striking, as yet hypothetical, consequence: Under appropriate conditions it leads to a parity-violating energy difference E_{pv} ^[10,11] between two enantiomers **R** and **L**, in thermodynamic terms, i.e. to a thermodynamic reaction energy $\Delta_R U_0^0$ different from zero

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[**] Based on the final part of the Hund/Klemm lecture ("Wie bewegen sich Moleküle?"; October 27, 1986) at the Max-Planck Institut für Festkörperforschung, Stuttgart (FRG). The main, first part will be published separately. The first Hund/Klemm lecture forms the basis of a review by H. Bock and R. Dammell in *Angew. Chem.* 99 (1987) 518; *Angew. Chem. Int. Ed.* 26 (1987) 504.

[***] If the foundations of life are dissymmetric, then because of dissymmetric cosmic forces operating at their origin; this, I think, is one of the links between the life on this earth and the cosmos, that is the totality of forces in the universe.

for the racemization: (a) (leaving the sign undetermined; see also appendix); $|\Delta_R U_0^0| \equiv |\Delta E_{PV}|$.

$L \rightleftharpoons R$ (a)

All of the above mentioned discussions of molecular chirality result in differing views about the actual "structure" (in a general, physicochemical sense) of chiral molecules and substances. These differences should not be dismissed entirely as problems in the realm of bad terminology or philosophy. Rather, we shall demonstrate that the different views correspond to different theories of chirality with conflicting predictions concerning the outcome of certain experiments. To decide unequivocally which theories must be dismissed, one must perform an experiment which discriminates between them. To date, there is essentially no experimental evidence available on some central questions and this aspect has been largely overlooked in the theoretical discussions of the problem. The present paper is intended to fill this gap. Some possible experiments^[50] will be discussed.

2. A Critical Discussion of Different Points of View Concerning Molecular Chirality

In this section we shall summarize some of the general aspects and predictions of the various theories of chirality. Predictions for specific experiments will be given in Section 3.

2.1. Macroscopic Molecular Models and Classical Mechanics: "The Classical Hypothesis"

The original description of chiral molecules was given in terms of molecular models that are the microscopic analogue of macroscopic models satisfying the laws of classical mechanics of our everyday world.^(1,18-21) It is in essence also the starting point of the organic stereochemists models. In modern language one would take the approximate Born-Oppenheimer potentials as true effective potential functions for the essentially classical motion of the heavy nuclei. These potentials may then either be symmetrical with respect to space inversion or there may be a slight asymmetry if there is a parity-violating term. In the former case the occurrence of left- and right-handed enantiomers arises from the initial conditions of a given experiment. It would arise quite naturally and is *not* difficult to understand. Because of the experimentally established energetic equivalence (to within rather large experimental error!) this was the historically prevalent point of view.⁽¹⁸⁻²¹⁾ *Pasteur* seems to have seriously considered also an intrinsic asymmetry. In this latter case enantiomerism would be rather similar to all other kinds of isomerism with a small $\Delta_R U_0^0$.

With the advent of quantum mechanics, governing also molecular vibrations and rotations, one might consider the classical point of view as irrelevant and superseded.⁽²⁻⁴⁾ However, one might also take an extreme outsider's point of view along the following lines: The motion corresponding to the interconversion of enantiomers in complex organic molecules is of very low frequency. It may be that for such

motions quantum mechanics becomes invalid, and classical mechanics (or something similar) is *intrinsically* valid (i.e. not just as an approximation to quantum mechanics). There is no computational test of sufficient accuracy in the quantum chemistry of enantiomers, which could disprove such a hypothesis. More interestingly, we are not aware of *any direct experimental test*. Such tests might search for either tunneling in the *symmetric* case (absent in classical mechanics) or look for direct violations of the quantum mechanical superposition principle, which is irrelevant for Newtonian mechanics both in the symmetric and asymmetric cases.

Before discussing specific experiments, it should be pointed out, that the "classical hypothesis" seems rather inconsistent and theoretically remote. There is no good reason for treating electrons and nuclei on a totally different footing, which is implied by taking the Born-Oppenheimer potentials as more than an approximate trick. In reality there is no good reason to assume that there are such potentials and one should consistently treat *both* electrons and nuclei by the same mechanics (quantum or classical). There is sufficient evidence for excluding a classical mechanical treatment for the electronic motions in enantiomers. One would thus be tempted to discard the classical hypothesis on theoretical grounds. In the absence of direct experimental tests, some might wish to resist this temptation.

2.2. The Quantum Mechanical Point of View with a Space Reflection Invariant Hamiltonian: "Hund's Hypothesis"

Hund⁽²⁴⁾ recognized that in quantum mechanics there will be a small splitting ΔE_+ due to tunneling between eigenstates of positive and negative overall parity, if the total hamiltonian H is invariant under space reflection for the potentially enantiomeric molecular system. The eigenfunctions of H would thus be achiral. Their superposition results in left- and right-handed enantiomers, which are *time dependent molecular states*. *Hund* estimated the time dependence for typical compounds and concluded that on ordinary time scales the tunneling contribution to interconversion would be negligible: The enantiomers are predicted to be kinetically stable.

In order to avoid certain confusions that sometimes arise, we should stress that there is no reason whatsoever to request that a molecule or chemical compound should correspond to an eigenstate of H . Many molecules are known to exist as kinetically stable entities, often even as scattering resonances in the continuum far above the ground state of H . A simple example is formaldehyde H_2CO , which is unstable with respect to decomposition into $H_2 + CO$, according to current thermodynamic data ($\Delta_R H_0^0 = -1.7 \pm 6 \text{ kJ mol}^{-1}$, a more pronounced example is $N_2H_4 = N_2 + 2 H_2$, $\Delta_R H_0^0 = -109 \text{ kJ mol}^{-1}$). These molecules are kinetically stable. In this context it may be useful to provide some orders of magnitude. The racemization of aspartic acid is among the fastest for amino acids and is believed to occur unimolecularly under certain conditions.^(56,60) At 310 K the rate constant is $k_{rac} \approx 2.7 \times 10^{-11} \text{ s}$, corresponding to a chemical relaxation time of about 1200 years. Most of the reaction occurs by thermal excitation over a barrier of about 125 kJ mol^{-1} .

Hund's hypothesis is perfectly consistent with all available experimental evidence. One may raise, however, some theoretical objections. The first, and certainly most serious one, concerns the influence of parity-violating perturbations due to the weak nuclear force. As this was only discovered in 1956,^[33-35] *Hund* could not know about it. In 1927 it seemed apparently too remote to even hypothesize about this possibility. Today we must take it into account.^[6,10,11,42-55] However, this does not automatically invalidate *Hund's* hypothesis for the fundamental structure and dynamics of enantiomers, whose properties depend critically on certain parameters, the splitting ΔE_{\pm} due to tunneling and the parity-violating splitting ΔE_{PV} (see appendix). Only when the inequality (1) holds will *Hund's* hypothesis be valid. Current theory would seem to exclude the inequality (1) for a number of typical cases.^[10,11] However, from an experimental point of view the question is open.^[50]

$$\Delta E_{\pm} \gg E_{PV} \quad (1)$$

The second objection was raised by *Pfeifer*.^[26] He points out that *Hund's* treatment neglects some interactions with the radiation field. If these are included, *Pfeifer* finds that the achiral eigenstates are removed and that the chiral states correspond to stable states of the system due to a superselection rule. Experimentally, this point also remains open.^[50]

The third and perhaps least serious objection comes from a discussion of collisional effects by *Harris* and *Stodolsky*.^[30] To the extent that at very low gas densities the idealization of a collision free molecule is adequate, this work complements *Hund's* work but does not reject his hypothesis (for a discussion of crystallization see Ref. [57]).

2.3. Influence of the Radiation Field: *Pfeifer's* "Superselection Rule Hypothesis"

Pfeifer pointed out two weaknesses of *Hund's* treatment.^[26,58,59] Firstly, *Hund* does not explicitly account for the apparent absence of "isomers of well defined parity".^[50] These would thus seem to be unstable or nonexistent, in contrast to the established high stability of enantiomers. This objection may or may not be taken seriously. Certainly the repeated statement^[58,27] that "according to experiment space reflection invariant pure states for enantiomeric molecules do not exist" is incorrect, as to the best of our knowledge no experimental evidence has ever been presented for the absence of states of well defined parity (there is no evidence for their existence either, but that is a different matter, see Section 3.1). Thus, *Hund's* treatment would seem to be somewhat incomplete but not necessarily incorrect. However, the first observation led *Pfeifer* to note that secondly, *Hund* omits to treat the interactions with the radiation field, which cannot be entirely removed. When *Pfeifer* includes these, he finds^[58] within the framework of algebraic quantum mechanics (see also Ref. [27]) a superselection rule, which, indeed, excludes on theoretical grounds the existence of states of well defined parity under certain conditions for enantiomeric systems. Thus, even without parity violating terms in the hamiltonian, the stable ground state of enantiomeric systems corresponds to left- and right-handed isomers and not to the symmetric state of positive parity.

Pfeifer's superselection rule certainly constitutes a most striking theoretical finding. He also gives some numerical estimates for molecules.^[26,58] However, there is no direct experimental test of the superselection rule hypothesis as yet.^[26,50] On the theoretical side, some aspects of *Pfeifer's* treatment have been revised or extended.^[2,7] One might also raise at least two general theoretical objections to *Pfeifer's* treatment:

1. *Maxwell's* equations and quantum field theory have equations of motion that are space reflection invariant, as is the molecular hamiltonian in the approximation used by *Pfeifer*. Thus from general symmetry considerations his result would seem undesirable, if not impossible.

2. It is not clear whether the infinite boundary conditions for the field used by *Pfeifer*, excluding gravitation, can correspond to any real physical situation or are meaningful idealizations. The two objections are related and we realize, of course, that the symmetry breaking is the essence of *Pfeifer's* theory. As the theoretical situation is not entirely clear, we would summarize that *experimentally* the question is definitely open.

2.4. The Stabilization of Enantiomers by Collision: "The Collision Hypothesis"

It has been suggested that interactions with some external medium, in particular also collisions in a gas, tend to stabilize enantiomers (**L** and **R**) and destabilize parity isomers ($+$ and $-$)^[30,31,32] (see also Ref. [59]). In discussing a Bloch type relaxation equation for the density matrix **P** of a two level problem in the $|L\rangle$ and $|R\rangle$ basis, *Harris* and *Stodolsky* derive the equation (2) for the relaxation to equilibrium for the population difference Δp of **L** and **R** (if $p_L^e \approx p_R^e$ for the equilibrium population p^e).

$$\Delta p(t) = P_{LL} - P_{RR} = \Delta p(0) \exp[-(\delta^2/\bar{\lambda})t] \quad (2)$$

Here, one has $\bar{\lambda}^{-1} \approx T_2$, the phase relaxation rate constant that can be assumed to be proportional to the collision frequency in a gas, and $\Delta E_{\pm} = 2\delta$, the tunneling splitting for the parity states, which can be related to the rate of racemization in the absence of collisions (Section 4). Equation (2) is assumed to hold in the case of strong damping, i.e. $(\bar{\lambda}/\delta) \gg 1$. One has the seemingly paradoxical result that the population relaxation rate $T_1^{-1} \approx \delta^2/\bar{\lambda}$ and thus the racemization rate constant k_{rac} are inversely proportional to the collision rate. But, normally, in the low pressure range of unimolecular reactions (of which racemizations are special cases) one has $k \propto$ collision rate, i.e. just the opposite behavior. This results from the mechanism of an ordinary unimolecular reaction, which involves a collisional activation process to energized states with fast reaction.^[60,70] The model of *Harris* and *Stodolsky* applies to the "low temperature limit" two state model of racemization only.

It is this starting point which one may criticize: In real polyatomic molecules, the two state model would apply only at exceedingly low temperatures $T \ll 1$ K, where all molecules are in the rotational and vibrational ground state. This will be difficult to achieve. A second criticism of the model comes from its neglect of the radiation field. One can

estimate that under dilute beam conditions thermal radiative transitions between ground and vibrationally excited states may be at least as important if not more so than transitions by collisions.^[50] Thirdly, as noted also by *Harris* and *Stodolsky*, there are cases of low collision rate and sufficiently fast inversion rate, where *Hund's* model would be applicable. One might then ask for the "structure" of the isolated molecule.

Whether or not the *Harris* and *Stodolsky* model is relevant to the stabilization or existence of long-lived enantiomers in dilute gases for real molecules at ordinary temperatures could be decided only by the direct experimental determination of the molecular relaxation parameters. To our knowledge, there exists no experimental evidence either supporting or denying this hypothesis. Thus, the theory merits an experimental test, possibilities for which will be discussed in Section 3.

2.5. Weak Nuclear Interaction and Parity Violation in Molecules

The first new aspect (after quantum mechanics and *Hund*) in terms of the *physics* of molecular chirality was certainly the discovery of the parity-violating weak nuclear force.^[33-35] Parity violation in physics in general and for chiral molecules in particular clearly was not foreseen by theoretical reasoning alone. Parity violation leads to a slight energy difference for the **L** and **R** isomers. Recent estimates on the basis of fairly detailed quantum chemical calculations place the parity-violating energy difference of enantiomers ΔE_{PV} in the range of 10^{-14} J mol⁻¹ or about 10^{-4} to 10^{-5} Hz in frequency units.^[10, 11] If this is accepted, the structure of enantiomers would be dominated by this energy difference. Tunneling from **L** to **R** would be quite negligible for typical molecules at low temperatures and the probability density for true molecular eigenstates associated mostly with one enantiomer (say **L**) would be negligible for that part of the configuration space associated with the other enantiomer (**R**). Optical isomers would then resemble ordinary isomers **A** and **B**, such as *cis-trans* isomers, separated by an energy difference ΔE_{AB} at the zero-point level. For these the eigenstates of the molecular hamiltonian are sufficiently well localized at low energies that they may be associated with one isomer only.

From the theoretical side this situation appears to be fairly well understood. However, there exists no experimental test yet. Clearly, a direct experimental measurement of the parity-violating energy difference would be in order.^[50] If the experimentally measured ΔE_{PV} were to be much smaller than the theoretical prediction, it might be that there are many optically active molecules, for which parity violation would be dynamically unimportant.

From a fundamental point of view the structural hypothesis of enantiomers based upon parity violation is the most interesting one, as it is based on symmetry arguments^[61] closely related to general conservation laws^[7, 11] following the thoughts of *A. E. Noether*. Understanding the structure of enantiomers in terms of the parity-violating energy difference by a quantitative measurement might have conse-

quences beyond physical stereochemistry in the realm of the physics of fundamental symmetries.^[50, 62]

2.6. Symmetry Breaking *de facto* or *de lege*

At this point it may be useful to distinguish the symmetry breaking through initial conditions in the ordinary classical (Section 2.1) or quantum (Section 2.2) theory from the symmetry breaking by *violation* of the fundamental symmetry law of parity conservation (Section 2.5).

If the initial conditions of a physical system can be chosen in different, but symmetrically equivalent ways, the symmetry of the *phenomena* or the actual state of motion will not necessarily reflect the underlying symmetry. A classical mass point moving in a symmetrical double well potential will be localized on one side, if it lies below the barrier of the double well. The direction of motion of the planets around the sun is well defined and does not reflect the symmetry of the law of motion or of space. The same is true for the **L** and **R** enantiomers in the classical situation or *Hund's* hypothesis. And a cigarette without filter will be lit at *one end*, even if it is symmetrical.

The symmetry of the underlying law or structure is broken *de facto* by the chosen initial conditions. But the underlying symmetrical law allows also the opposite, *symmetrically equivalent* solution. In the quantum case (Section 2.2) one has then the interesting possibility of a symmetrical state of motion by the superposition principle, but such a symmetrical state is no more likely than the asymmetrical state. In classical mechanics this symmetrical state does not exist, as the superposition principle is lacking.

If, however, the symmetry is already broken in the underlying law of motion (asymmetrical double well for the classical mass point, parity violation for **L** and **R**, cigarette with a filter), then the two states of motion are not symmetrically equivalent, and we speak of symmetry breaking *de lege*. If the symmetry breaking *de lege* is small, then in quantum mechanics a very nearly symmetrical state can be generated by linear superposition, which will evolve slowly in time with respect to its symmetry properties (time-dependent symmetry violation).

These two situations of symmetry breaking *de facto* and *de lege* are obviously quite different and should be distinguished by appropriate terminology, as proposed. There is a third class of symmetry breaking, which is commonly named "spontaneous".^[63] It arises with an intrinsically symmetrical dynamical structure and *Pfeifer's* hypothesis is an example of this. One might add that one view of parity violation introduces this as a spontaneous symmetry breaking in a cosmological context. Thus, the parity-violating molecular hamiltonian of our present world arises as a particular solution out of a fundamentally symmetrical situation at the origin of our universe. It may be that the **L** isomer of a given molecule is more stable than the **R** isomer in our world; this view implies that another world may exist in which the reverse would be true. This view of parity violation is nevertheless consistent with the statement that the left-right symmetry-breaking in our world is *de lege*, as the laws of motion are now defined in the present context.

2.7. "Totaliter aliter"

Before discussing experiments discriminating between current hypotheses of the structure of chiral molecules, one should consider the possibility that the experimental result will contradict *all* current hypotheses and is thus "totally different" (totaliter aliter⁽⁶⁴⁾). Such a discussion must necessarily be speculative, as otherwise we could have listed yet another, specific alternative. Effects that have not been considered so far and that may influence the structure of chiral molecules are time reversal symmetry violation and gravitation. Both are very small at the molecular level, but one is talking about small effects anyway. At the other end of the spectrum one has configuration interaction of the molecular low energy states with excited electronic states and dissociative states that are achiral. This might influence the ΔE_{\pm} in an unpredicted way, as it is usually calculated as a tunneling splitting in the electronic ground state. At still higher energies there are states, where the particle concept (electrons and nuclei) of molecular structure is no longer useful. The effects of configuration interaction with such high energy field states (including increasing numbers of positrons, antiprotons etc.) are small, but not easy to predict and may perhaps lead to surprising consequences for the very small energy effects that we consider in chiral molecules. Finally, there might be effects from an as yet unknown force.

Even this list is not complete. Together with the five specific alternatives mentioned before it should convince the reader, that no definite statement on the structure of chiral molecules will be possible without direct experimental tests, even if *some* of the theoretical alternatives may seem remote or might even be excluded as inconsistent with currently established facts by a sufficiently careful analysis.

3. Experimental Tests

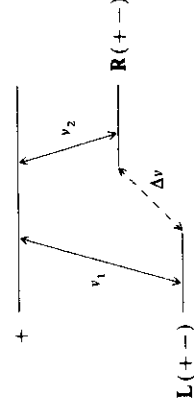
We shall discuss possible experimental tests of the hypotheses, labeled 1–5 following the order of Section 2. In each case we shall discuss the *principle* of the experiment, not the details of its realization, which are complex and often not obvious, and its capabilities to distinguish between the various hypotheses.

3.1. The Principles of the Experimental Testing of Various Hypotheses Concerning Molecular Chirality

1. The first class of experiments concerns the spectroscopy of separate enantiomers. Proposals and actual experiments of high accuracy have been communicated in the radiofrequency and infrared ranges. If the weak nuclear force has sufficient influence, the absorption frequencies for the individual **R** and **L** isomers will be slightly different. Measurements with CO₂ lasers have been attempted on CHFClBr by *Kompanets et al.*⁽⁴³⁾ but gave a null result. Experiments on camphor by *Arimondo et al.*⁽⁵²⁾ gave the same absorption frequencies for **D** and **L** to an accuracy $\Delta\nu/\nu$ of 10^{-8} , probably still far away from an expected effect, although no accurate calculations have been carried out. Calculations for NMR chemical shifts predict differences of

about 1 mHz, which may be measurable but have not yet been proven experimentally.^(47–49) If successful, these experiments are, in principle, able to discriminate the inversion symmetrical hypotheses 1–4 from the asymmetrical 5. They do not give, however, a direct measure of the parity-violating energy difference of enantiomers ΔE_{PV} . We note that in atomic spectroscopy the search for effects from the weak nuclear force has been successful,^(39–41) and for diatomic molecules there are some null results available in searches for both parity and time-reversal symmetry-violation.^(51,53,54)

2. The second class of experiments concerns spectroscopic transitions *between* the **R** and **L** isomers. When ΔE_{PV} is much larger than the splitting due to tunneling, one-photon transitions (at mHz frequencies) are strictly forbidden. However, a two-photon transition with an intermediate state of well defined parity will be allowed according to the following scheme:



Scheme 1. Two-photon transfer between the enantiomers **R** and **L**.

Possible transitions in this case may involve an excited electronic state that is achiral and has rovibronic levels of well defined parity. The corresponding transitions would occur in the visible or UV part of the spectrum.

Stabilizing two lasers at the transition frequencies ν_1 and ν_2 of the **L** and **R** isomers one could measure the beating between them, which may occur on the time scale of hours. This experiment is technically very difficult as it requires long time stabilization of the frequency to within $\Delta\nu/\nu \approx 10^{-19}$, quite apart from other difficulties. A slightly more favorable situation would occur for special molecules, having a small tunneling splitting ($\Delta E_{\pm} \ll \Delta E_{PV}$) in the vibrational ground state and a large one ($\Delta E_{\pm} \geq \Delta E_{PV}$) in a vibrationally excited state of the electronic ground state. Scheme 1 would then allow a measurement in the IR with a gain of a factor of about ten concerning the required accuracy. In even more special cases, it may be possible to measure the highly forbidden transition **L** \leftrightarrow **R** at the frequency $\Delta\nu$ directly. This will happen, when tunneling is just sufficient to mix the **L** and **R** wave functions slightly, still preserving the dominant asymmetry. The **L** \leftrightarrow **R** transition will then be slightly allowed as it acquires a weak inversion transition character. Of course, such optical isomers are necessarily rather short-lived, and are not the most typical cases. The second class of experiments allows us to measure ΔE_{PV} and thus to decide to what extent inversion, or, symmetry is violated *de lege* or not (i.e. preferring hypothesis 5 to the others).

3. A third class of experiments is somewhat speculative at present. It would be based on the kinetic selection of **L** and **R** isomers due to the asymmetric kinetics in the case of an appreciable ΔE_{PV} :



$$\frac{k_{RL}}{k_{LR}} = 1 \pm \bar{J} \quad (3)$$

but in relation with nonequilibrium kinetic schemes in evolutionary times, mechanisms have been discussed that would lead to a measurable selection of **L** or **R**.^[7-9, 12] If a mechanism of this kind could be found for a quantitatively well understood laboratory reaction, the measured selection rate for **L** or **R** could be interpreted in terms of $\bar{\Delta}$ and finally ΔE_{pv} . Such an experiment would be an outstanding achievement in chemical kinetics, but at present there are no ideas as to how it could be realized. It might also be possible to unravel the mechanism of the natural selection of optical isomers in prebiotic times from fossil documents and thereby obtain the relevant parameters. Again this is at present a remote possibility. If ever such evaluations became possible they would discriminate hypothesis **5** against the others and, perhaps, provide a result for ΔE_{pv} in certain molecules.

4. Another experiment has been proposed, which is based on the generation of states of well defined parity and the observation of the time dependence of parity.^[50] The principle of the experiment is based on three steps: a) Preparation of molecular states of well defined parity (for instance (+) from optically active molecules (**R** or **L**) of ill defined parity in the electronic ground state. b) Free evolution of the isolated molecule with initially well defined parity (+). Under this condition the probability for negative parity will increase quadratically with time; for short times Equation (4) holds.^[50] For long times one has an oscillation with period τ [Eq. (5)].

$$p_- = (\pi \Delta E_{pv} t / h)^2 \quad (4)$$

$$\tau_{\pm} = h / \Delta E_{pv} \quad (5)$$

c) Spectroscopic observation of the population of states of the "forbidden" parity (for example p_-) as a function of time. According to Equations (4) or (5) one can evaluate ΔE_{pv} and again distinguish hypothesis **5** from the others. This experiment allows us, however, also to decide between hypothesis **2** and **1** or **3**. In the preparation step [Eq. (6)] of the experiment one generates a linear superposition state χ_+ [Eq. (6)].

$$\chi_+ = (\lambda + \varrho) / \sqrt{2} \quad (6)$$

where λ and ϱ are the eigenfunctions of the **L** and **R** isomers (cf. Appendix). According to the quantum mechanical superposition principle this is always possible whether or not there is a sizeable ΔE_{pv} (hypotheses **2** and **5**). According to the classical hypothesis **1** or the superselection rule hypothesis **3**^[26] the preparation step will generate only **R** or **L** or mixtures of **R** and **L**. These can be distinguished experimentally from the χ_+ state by the dipole absorption spectrum. χ_+ has only strong electric dipole absorptions to states of negative parity whereas **L** and **R** and mixtures have strong electric dipole absorption to both positive and negative rovibronic states. Thus, in an appropriate electronic transition, for example,^[50] hypotheses **1** and **3** would predict a spectrum with about twice as many lines than predicted by hypotheses **2** and **5**. The experiment provides a direct test of the superposition principle for enantiomers. It would not allow one to differentiate between hypotheses **1** and **3**, which both require violation of the quantum mechanical superposition principle

pic. Hypothesis **1** is in a sense a very general hypothesis and **3** might be thought to be a special, precise formulation. In that sense a distinction between **1** and **3** would become meaningful only if precise alternatives were formulated. This class of experiments would be a test for all possible hypotheses except **4** and is thus very powerful. We have also discussed in detail^[50] that the experiment should be practical, even if difficult and expensive in its setup. Although the experiment is subject to numerous obvious complications, the evidence presented in Ref. [50] and further investigations^[65] all suggest that the experiment can be realized with a guarantee of a definite outcome, whichever this may be. Complications could arise if ΔE_{pv} is either very small or much larger than currently predicted. If ΔE_{pv} is very small, from the absence of parity evolution one could then only derive an upper limit on ΔE_{pv} . If ΔE_{pv} is very large, the oscillation of parity might be so fast that it would simulate an **L-R** mixture, leading to the incorrect conclusion that hypotheses **1** or **3** are appropriate. By increasing time resolution, it should be easy to avoid such an error. Also, a very large ΔE_{pv} would be easily measured by a class 2 experiment and if established, proper precautions could be taken. We might also mention that the technique of *Kukolich et al.*^[68] could be useful in the realization of our experiment (see also the related discussion below). Another realization involving excited electronic states is sketched in Figure 1.^[50]

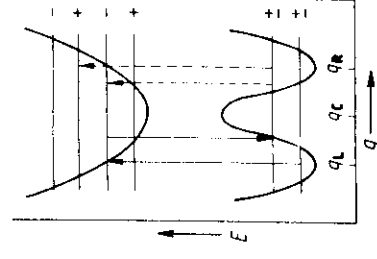
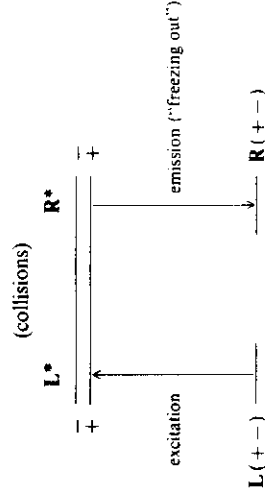


Fig. 1. Scheme for the generation of states of well defined parity (if possible) in a molecule that is chiral in the electronic ground state. The ground state potential has a high barrier for racemization; the excited state a low barrier or none as shown. q = inversion coordinate. In a first optical transition (1) one generates a state of well defined parity (+) in the excited state; and in the second (2) in the ground state. The dashed lines indicate the spectroscopic observation of the outcome of the experiment (after Ref. [50]).

5. The final class of experiments would test the collisional hypothesis **4** perhaps by observation of the time dependence of optical activity.^[30] A nontrivial time depending enantiomers, be observed for rather quickly interconverting enantiomers, according to current estimates of ΔE_{pv} . A possible realization of the experiment would follow Scheme 2.

In a molecular beam of stable **L** and **R** isomers a pump laser would be used to excite the **L** isomer, for example, to an electronic or vibrational state in which the splitting due to tunneling is sufficient to allow interconversion at an observable rate, ideally complete inversion to **R** within a time of free flight in the beam. This transformation could be followed as a function of the length of flight along the beam by measuring the optical activity by Raman scattering^[66] perhaps with CARS or Fourier transform techniques^[67] in or-



Scheme 2. Experiment for testing the collision hypothesis 4 via the time dependence of the optical activity.

der to increase sensitivity (a serious problem in measuring optical activity). One might also increase sensitivity by freezing out the transformed molecules with a dump laser and collecting the stable "product" **R** for some time until sufficient material for the experimental sensitivity is available. In the free evolution stage of the experiment p_+ and p_- would remain constant and p_R and p_L would oscillate as suggested by *Harris* and *Stodolsky*. According to their prediction, this oscillation should be *slowed down* if we allow for collisions with some background gas in the molecular beam chamber. One needs just to investigate the $L \rightarrow R$ interconversion as a function of gas pressure, using Equation (2) for the evaluation of the relevant parameters. If the effect predicted by *Harris* and *Stodolsky* is observed, their hypothesis 4 would be confirmed for the molecular system in question, and one might, by systematic investigations, obtain an understanding of the circumstances in which the collisional stabilization of enantiomers is relevant (see also Section 4). A complication will arise in all these experiments, because a real molecule is not a two level system and even if the initial state is a coherent superposition of just two states, collisions will tend to transfer excitation to other states. It may also be useful to study the $L \rightarrow R$ oscillations by observations of quantities other than optical activity. A promising technique could be based upon the experiment of *Kukolich* et al.,^[68] who studied collision cross sections of parity states ($-$) and of superposition states ($+ -$) in ammonia. They used the measurement of polarization in a microwave cavity (their case 2 experiment), which may be more sensitive than the measurement of optical activity. Indeed this experiment could be carried out in a very imaginative way in selected high J, K states of *near* symmetric tops with almost oriented molecules:



As indicated by the dipole moment arrows in Equation (c), the $L \rightarrow R$ interconversion in an oriented molecular beam will change the macroscopic electric dipole moment orientation and this could be detected. The dynamic situation can again become very complex with collisions.^[69]

We have shown in this section that meaningful *real* experiments (as opposed to thought experiments) could test the different hypotheses on the structure of enantiomers. The hypotheses provide significantly different predictions for the various experiments. An appropriate combination of the different experiments discussed here would allow us to exclude all but one of the hypotheses, but we do not know which one

would remain intact, even though intuition may suggest one. As discussed in Section 2.7, perhaps none of the hypotheses would survive the test, but this appears unlikely. At present, to the best of our knowledge, there is no definite experimental evidence available whatsoever. It should be obvious that the outcome of the experiments will depend in general also upon molecular parameters. Different hypotheses may therefore be correct for different molecules. It is then in order to discuss the scope of these hypotheses to make predictions concerning the influence of molecular parameters.

3.2. The Influence of Molecular Parameters

Molecular properties can influence considerably the nature of chirality in a given molecule. The most obvious case in question arises for *Hund*'s hypothesis and the parity-violation hypothesis. The inequality (1) determines which one applies. We have fairly standard techniques to estimate ΔE_+ , although it may sometimes be difficult to calculate the reaction path and barrier height for racemization by accurate ab initio techniques. The calculation of ΔE_{PV} by ab initio methods has just started.^[10, 11] It is not clear yet (to the author) to what extent one can be certain that all the important effects have been included in the calculations. In this sense, too, an experimental test would be important. If current theoretical results are accepted, one would be able to calculate the relevant parameters in inequality (1) for simple molecules. More investigations of ΔE_{PV} are needed.

The classical hypothesis (1) is, at present, purely qualitative. *Pfeifer* has tried to make some estimates, for which molecular parameters his superselection rule should be applicable.^[26, 58] The problem deserves more quantitative theoretical investigations.^[27] The interested experimentalist would like to know from the theoretician, for which molecules and at what energies the symmetry breaking phase transition occurs, if it happens at all. Probably the isolated two-level approximation has to be abandoned for realistic estimates.

Harris and *Stodolsky*^[30] have provided a collision theory formulation for their hypothesis. So far, no one has actually calculated quantitative cross sections for specific examples. Before planning experiments, such calculations would be helpful. The most serious problems will arise from the multistate nature of real molecules. That is, a large multichannel scattering calculation will be required, even if many channels are closed.

For the purpose of estimating collisional effects on the various doublet states of enantiomers, one may consider the results on ammonia inversion sublevels.^[68] Here it is found that in the basis of parity states effective cross sections for T_1 and T_2 processes are somewhat larger than gas kinetic values and of about the same order of magnitude in inert gas collision partners, T_1 being shorter than T_2 with dipolar collision partners. This can be understood by a mechanism of dipolar relaxation connecting the parity sublevels but not the $R-L$ sublevels. One can show that for a *degenerate* two-level problem, T_1 for the parity basis χ corresponds to T_2 for the $q-\lambda$ basis (see Appendix). Extrapolating from these results one would thus assume fast, approximately gas kinetic phase relaxation for the density matrix in the (q, λ) basis and fast

Table 1. Some chiral molecules of particular theoretical or experimental interest.

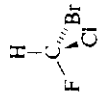
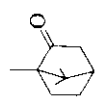
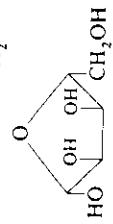
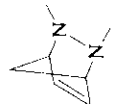
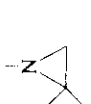
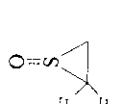
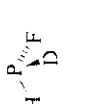
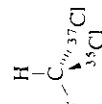
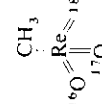
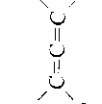
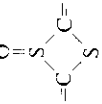
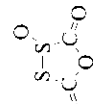
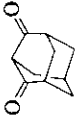

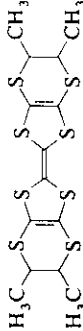
Molecule	Name	Remarks and references
		volatile, gas phase spectroscopy [43] possible: IR-laser chemistry
	camphor	(volatile) gas phase spectroscopy [52]
$\text{H}_3\text{C}-\text{CH}(\text{NH}_2)-\text{CO}_2\text{H}$	alanine	theory: $\Delta E_{\text{PV}}^{\text{max}} \approx 10^{-13} \text{ J mol}^{-1}$ (L more stable [10, 11])
$\text{HO}_2\text{C}-\text{CH}_2-\text{CH}(\text{NH}_2)-\text{CO}_2\text{H}$	aspartate	theory: $\Delta E_{\text{PV}}^{\text{max}} \approx 8 \times 10^{-14} \text{ J mol}^{-1}$ (L more stable [11]); well known racemization rate [56]
	ribose	theory: $\Delta E_{\text{PV}} \approx 2 \times 10^{-14} \text{ J mol}^{-1}$ (D more stable [11]) relativistic theory $\Delta E_{\text{PV}} \approx 10^{-8} \text{ J mol}^{-1}$ [49] relativistic theory [49] $\Delta E_{\text{PV}} \approx 10^{-7} \text{ J mol}^{-1}$ calculated difference in NMR chemical shift of enantiomers $\approx 1 \text{ mHz}$ [47, 48]
$\text{H}-\text{Te}-\text{H}$ (hypothetical structure, twisted 90°)		suitable for spectroscopy
$\text{Pt}(\text{C}_2\text{H}_5)_2$ (hypothetical structure)		modest barrier, NMR spectroscopy [91]
$[\text{CHCl}_2\text{CH}_2\text{TIH}]^\ominus$ (hypothetical structure)		modest barrier [90], expected low barrier in excited electronic states vibrational and electronic spectroscopy. Higher barriers with NCI [92]
	<i>N,N</i> -dimethyl-2,3-diazabicyclo[2.2.1]hept-5-ene	modest barrier, laser chemistry and spectroscopy
	1,2,2-trimethylaziridine (also 1 <i>H</i> -aziridine and oxaziridines)	intermediate barrier, spectroscopy and IR laser chemistry (similar also PX_3)
	(general sulfoxides)	isotopic chirality, very small ΔE_{PV} expected
	(general phosphanes)	isotopic chirality, suitable for spectroscopy in jets and overtones [93], very small ΔE_{PV} expected
$\text{CHD}=\text{C}=\text{CHD}$	dideuteroallene	isotopic chirality with heavy atom, volatile compound for spectroscopy [94] and laser chemistry
		hypothetical spinless chiral molecule
		hypothetical spinless chiral molecule (also related derivatives)
		hypothetical spinless chiral molecule [96]
		dynamic chirality [88] locally CH^* excited dynamical chirality (Section 4)
		
$\text{DFC}=\text{C}=\text{CH}^*\text{H}$	allene (vibrationally twisted)	

Table 1. (Continued)

Molecule	Name	Remarks and references
	adamantanedione	proposed dynamical (electronic) chirality [86]
	methane	dynamic chirality of certain levels (Section 4)
		basis for chiral conductor [95], macroscopic electronic effects in ΔE_{PV} ?

population relaxation in the χ_+ , χ_- basis. On the other hand, by the same argument as for other isomerizations with high barriers, one would assume slow population relaxation T_1 in the (ρ, λ) basis. This would easily explain why the "isomers of well defined parity" are not normally found in nature (*Primas'* paradox): They are collisionally unstable and equilibrate at about the gas kinetic collision rate. The arguments given above for collisions hold also for thermal background radiation, which will probably, via vibrationally excited states, quickly interconvert the + and - isomers but not **L** and **R**.^[50] Quantitative experimental results on these cross sections are lacking, however, and would be obtained by a combination of experiments of type (4) and (5). Thus, some of the experiments discussed in Section 3.1 would provide information on molecular stationary state, collisional and radiative kinetic properties.

For carrying out spectroscopic experiments on the foundations of molecular chirality, it may be useful to choose from a list of suitable molecules. Criteria are: 1. Simplicity (few atoms); 2. volatile compounds; 3. heavy nuclei (for a large ΔE_{PV}); 4. a limited number of nuclei with spin (perhaps a "spinless" molecule, except for the NMR experiments) in order to remove close degeneracies in the spectra; 5. for some investigations molecules with modest energy barriers for racemization. Table 1 summarizes some molecules that may be considered, including a few for which ΔE_{PV} has been calculated. In a search, it transpired that "spinless" enantiomeric compounds are not known, and some are proposed to stimulate the imagination of the synthetic chemist.

4. The Kinetics of Racemization

Molecular structures are in general time dependent and thus an understanding of the dynamics of chiral molecules and of the kinetics of racemization is required in relation to their structural properties. Racemization reactions are a special class of isomerization reactions, which can be dealt within the framework of unimolecular rate theory.^[70] Under ordinary "high temperature" conditions they can be discussed approximately in terms of a quasiclassical barrier crossing in the theory of reversible unimolecular reactions^[72] or, even more simply by the kinetic scheme in Eqs. (b) and (3) with a very small Δ . The rate constants will follow the Arrhenius law (7).

$$k_{RL} \simeq k_{LR} \simeq A \exp(-E_A/RT) \quad (7)$$

Another limit is the symmetrical two level tunneling model of racemization which does not lead to kinetic equations but to oscillatory motion.^[24] The period of oscillation ($\Delta E_{PV} \simeq 0$) is given by Equation (8).

$$\tau = h/\Delta E_{\pm} \quad (8)$$

These descriptions are textbook material in the realm of kinetics^[60] or of spectroscopy ("ammonia inversion").^[73] The treatment of *Harris* and *Stodolsky*^[30] extends the "low temperature" two-level tunneling model to cases involving parity violation and collisions. We shall not discuss these simplified models further but rather refer to the extensive literature on this subject.

Closer inspection of the dynamics of racemization shows, however, that it has certain very special features because of the *approximate* nonrigid molecular symmetry of space inversion and energy equivalence of **L** and **R** isomers.^[71, 74-76] These special kinetic properties have not been discussed before for real chiral molecules at finite energies, where, in general, a very large number of quantum states renders statistical approximations useful.^[77] We shall consider the strongly quantized case at energies below the classical energy barrier. Here, the reaction is dominated by quantum tunneling and quasiclassical barrier crossing is not a useful concept. In this case, the molecular spectrum shows close degeneracies associated with the interplay of ΔE_{PV} and ΔE_{\pm} and the average spacing of molecular states $\delta = \rho^{-1}$ (ρ = density of rovibronic or nuvibronic states subject to symmetry constraints^[76]). This situation leads to very peculiar kinetic properties, depending on these three parameters. Similar behavior is expected for other isomerizations with a very small energy difference between reactant and product states, but in the case of chiral molecules it is essential for symmetry reasons and it thus reveals some of the fundamental properties of chiral molecules. We shall discuss some simple limiting cases of the kinetics of racemization in turn. We start by disregarding collisional and radiative transitions and give a phenomenological discussion of their effects at the end.

The experimental situation that one should have in mind in the following discussion of racemization of an ensemble of isolated molecules is a cold molecular beam in high vacuum, for instance a supersonic jet, excited to some energy $E \pm \Delta E$, for instance with a laser, such that $\Delta E \gg \delta$ but $\Delta E \ll E < E_0$ (classical threshold for racemization). We shall thus calculate the statistical, microcanonical racemization rate under these conditions. Thermal rate constants can be derived from this.

If an ordinary microcanonical equilibrium were obtained in these racemizations, it would be governed by the densities of states ϱ of the **R** and **L** enantiomers. In order to get an estimate for this we may use a semiclassical approximation for the harmonic density of states [Eqs. (9) and (10)]^[70] and neglect to a first approximation the differences between the frequencies $\nu_1^{\mathbf{R}}$ and $\nu_1^{\mathbf{L}}$ of the isomers (but not ΔE_{PV}).

$$\varrho_{\mathbf{L}} = \frac{(E + aE_2^{\mathbf{L}})^{s-1}}{\prod_1 \hbar \nu_1^{\mathbf{L}}} \quad (9)$$

$$\varrho_{\mathbf{R}} = \frac{(E + aE_2^{\mathbf{R}} + \Delta E_{\text{PV}})^{s-1}}{\prod_1 \hbar \nu_1^{\mathbf{R}}} \quad (10)$$

Hence, with s vibrational degrees of freedom, and with vibrational zero point energies $E_2^{\mathbf{L}} \approx E_2^{\mathbf{R}}$ and vibration frequencies $\nu_1^{\mathbf{L}} \approx \nu_1^{\mathbf{R}}$ one gets, setting $E' = E + aE_2$ (with an energy dependent "constant" $0 \leq a \leq 1$) the Equations (11) and (12).

$$K_{\text{micro}} = \frac{K_{\mathbf{R}\mathbf{L}}^{\text{micro}}}{K_{\mathbf{L}\mathbf{R}}^{\text{micro}}} \approx \left(\frac{E' + \Delta E_{\text{PV}}}{E'} \right)^{s-1} \quad (11)$$

$$\ln(K_{\text{micro}}) = (s-1) \ln \left(1 + \frac{\Delta E_{\text{PV}}}{E'} \right) \approx (s-1) \frac{\Delta E_{\text{PV}}}{E'} \quad (12)$$

Thus, with $\Delta E_{\text{PV}} \ll E'$, K_{micro} will deviate very little from 1 (say, typically, by 10^{-18}). The actual situation is more complicated.

4.1. "Fast Tunneling" with Negligible Parity Violation and Small Densities of States

The time evolution for the isolated chiral molecule is governed by the differential equation (13) for the time evolution operator U ,^[78] which solves the time-dependent Schrödinger equation for Ψ and the Liouville-von Neumann equation for P according to equations (14)–(16).

$$i\hbar \frac{\partial U}{\partial t} = \mathbf{H} U \quad (13)$$

$$U(t) = \exp(-i\mathbf{H}t/\hbar) \quad (14)$$

$$\Psi(t) = U(t)\Psi(0) \quad (15)$$

$$P(t) = U(t)P(0)U^\dagger(t) \quad (16)$$

$\Psi(t)$ is the wave function of a molecule and $P(t)$ the density operator of an ensemble, respectively. In order to consider racemization or the time dependence of optical activity, we could write these equations as matrix equations in the basis of molecular states of well defined handedness (ϱ_i and λ_i). These are not generally eigenstates of \mathbf{H} and thus the matrix representation of \mathbf{H} will contain off-diagonal contributions. One can calculate these off-diagonal contributions by means of the Born Oppenheimer approximation in terms of a tunneling through the potential barrier, but this is by no means a necessary or exact description of the problem and is

given here only for visualization. If the rovibronic density ϱ of molecular states is low [inequality (17)],

$$\delta = \varrho^{-1} \gg \Delta E_{\pm}, \Delta E_{\text{PV}} \quad (17)$$

the total hamiltonian matrix is approximately block diagonal, with two dimensional blocks of the form (18),

$$\mathbf{H}^{(2)} = \begin{pmatrix} \langle E_{\mathbf{k}} \rangle - \Delta E_{\text{PV}}/2 & \Delta E_{\pm}^{(\mathbf{k})}/2 \\ \Delta E_{\pm}^{(\mathbf{k})}/2 & \langle E_{\mathbf{k}} \rangle + \Delta E_{\text{PV}}/2 \end{pmatrix} \quad (18)$$

$\langle E_{\mathbf{k}} \rangle$ is the average diagonal energy of the \mathbf{k} th two-dimensional block. We shall make use of circular frequencies instead of energy parameters [Eqs. (12) and (20)].

$$D_{\mathbf{k}} = 2\pi \Delta E_{\pm}^{(\mathbf{k})}/\hbar \quad (19)$$

$$A_{\mathbf{k}} = 2\pi \Delta E_{\text{PV}}^{(\mathbf{k})}/\hbar \quad (20)$$

Suppose we have an equal initial population in N quantum states of the pure **L** isomer [Eq. (21)].

$$P_{\mathbf{L}}(0) = \sum_{j=1}^N P_{j(\mathbf{L})}(0) = 1 \quad (21)$$

The time evolution of the population of the **R** isomer is given by (22) (cf. Ref. [77] and Appendix).

$$P_{\mathbf{R}}(t) = N^{-1} \sum_{i=1}^N \frac{D_i^2}{D_i^2 + A_i^2} \left[\sin \left(\frac{t}{2} \sqrt{D_i^2 + A_i^2} \right) \right]^2 \quad (22)$$

We consider now the special case $D_{\mathbf{k}} \gg A_{\mathbf{k}} \approx 0$. In practice this applies always at high energies, with large tunneling frequencies (say 10^6 s^{-1} or more); one then obtains (23).

$$P_{\mathbf{R}}(t) \approx N^{-1} \sum_{i=1}^N \left[\sin \left(\frac{D_i t}{2} \right) \right]^2 \quad (23)$$

The D_i at energy $E \pm \Delta E$ will vary widely. For states that are highly excited in the coordinate associated with the tunneling motion, D_i will be large, for other states it will be small. This situation is well known for the case of ammonia, where excitation of the NH stretching modes increases the inversion splitting only slightly.^[73] Even if the coupling of vibrational modes is large, at high energies, the most reasonable assumption would be that the D_i are randomly distributed according to some distribution function $G(D)$ with the average $\langle D_i^2 \rangle \langle E \rangle$ increasing with molecular energy E . If N is very large, we can replace the sum in Eq. (23) by an integral, neglecting terms of the order $1/N$ [Eq. (24)].

$$P_{\mathbf{R}}(t) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dD G(D) [\sin tD/2]^2 \int_{-\infty}^{\infty} dD G(D) \quad (24)$$

In this description, the detailed rovibrational molecular dynamics is contained in the spectral distribution function $G(D)$. Little is known as to what this may be. We shall

consider two possible assumptions: (25) and the Lorentz function (27). From (25) we get (26), while (27) gives (28).

$$G(D) = \begin{cases} \text{constant,} & -D_{\max} < D < D_{\max} \\ 0 & \text{otherwise} \end{cases} \quad (25)$$

$$p_{\mathbf{R}}(t) = \frac{1}{2} \left[1 - \frac{\sin(D_{\max} t)}{D_{\max} t} \right] \quad (26)$$

$$G(D) = D_{\mathbf{L}} / (\pi(D^2 + D_{\mathbf{L}}^2)) \quad (27)$$

$$p_{\mathbf{R}}(t) = \frac{1}{2} [1 - \exp(-D_{\mathbf{L}} t)] \quad (28)$$

Both approaches give an approximate relaxation to the excited microcanonical equilibrium ($t \rightarrow \infty$) $p_{\mathbf{L}} \approx p_{\mathbf{R}} \approx 1/2$ (for $\Delta E_{\text{PV}} \rightarrow 0$). Only in the second case is this relaxation truly exponential with a chemical relaxation time $\tau_{\mathbf{R}} = 1/D_{\mathbf{L}}$. Real distribution functions for D will probably be characterized by some maximum value D_{\max} , such as in Equation (26), corresponding to the one-dimensional model with a tunneling splitting D_{\max} calculated with *all* the energy in the racemization mode. One can develop detailed models for $G(D)$. The main result here is that in real, excited molecules under the conditions discussed *one will observe relaxation to zero optical activity even without collisions*. This is in contrast with the two-level prediction of oscillatory optical activity. Before discussing other limiting cases we should give typical experimental conditions, in which the present case will apply. For a molecule SOFCI after IR multiphoton excitation or a molecule such as $(\overline{\text{CF}}_2\text{NClCH}_2)$ after overtone laser excitation of CH modes one will expect such a behavior. The density of states is still quite small and the tunneling splitting can always be made sufficiently large ($D \gg \Delta$) by adequate excitation. Racemization in the beam can then be sufficiently fast (ns to ms time range) that both collisions and spontaneous and thermally induced radiative transitions are negligible: we are talking about conditions that may prevail in real experiments. In principle, one can also excite selectively one pair of tunneling levels and observe oscillatory dependence, but this is less important in practice.

4.2. Large Parity-Violating Energy Difference ΔE_{PV} and "Slow Tunneling", with a Small Density of States

Current calculations suggest that, at low energies, ΔE_{PV} will exceed ΔE_{\pm} in chiral molecules. As long as Equation (17) is satisfied, we still obtain the block diagonal structure of \mathbf{H} as given by Equation (18). By the arguments given in Section 4.1 one obtains from Equation (22) with normalized distribution functions $F(\Delta)$ and $G(D)$ Equation (29).

$$p_{\mathbf{R}}(t) = \int_{-x}^{+x} \int_{-x}^{+x} dF(\Delta) \int_{-x}^{+x} dDG(D) \frac{D^2}{D^2 + \Delta^2} \left[\sin \left(\frac{t}{2} \sqrt{D^2 + \Delta^2} \right) \right]^2 \quad (29)$$

ΔE_{PV} is essentially an electronic property depending upon the electronic wave function at the positions of the nuclei.^[6,10,11,45,49] Although this certainly depends on the rovibrational state, it makes sense to take it as being constant, particularly for rigid molecules without large amplitude motions (except for racemization). The distribution

function $F(\Delta)$ is thus approximately a Dirac delta distribution $\delta(\Delta - \Delta_c)$. On the other hand, D will vary in a wide range from D_a to D_b , as discussed before. In order to obtain a simple result we assume that (30) applies.

$$G(D) = \frac{\sqrt{D^2 + \Delta_c^2}}{N_0 D} \text{ for } D_a < D < D_b \quad (30)$$

with N_0 as normalization constant, so that $\int_{-\infty}^{+\infty} G(D) dD = 1$.

$$N_0 = \sqrt{D_b^2 + \Delta_c^2} - \sqrt{D_a^2 + \Delta_c^2} - \Delta \ln \left\{ \frac{D_a(\Delta + \sqrt{D_b^2 + \Delta_c^2})}{D_b(\Delta + \sqrt{D_a^2 + \Delta_c^2})} \right\} \quad (31)$$

For $\Delta_c \ll D$ one obtains a constant distribution and results equivalent to Equation (26). For $\Delta_c \gg D$, $G(D)$ is proportional to $1/D$ (assuming positive D_a and D_b). One obtains Equation (32).

$$p_{\mathbf{R}}(t) = \frac{1}{2N_0} \left\{ \left(\sqrt{\Delta_c^2 + D_b^2} - \sqrt{\Delta_c^2 + D_a^2} \right) - \frac{1}{t} \left[\sin(t\sqrt{\Delta_c^2 + D_b^2}) - \sin(t\sqrt{\Delta_c^2 + D_a^2}) \right] \right\} \quad (32)$$

As $t \rightarrow \infty$ this relaxes, with some oscillations, to a stationary value [Eq. (33)].

$$p_{\mathbf{R}}(\infty) = \frac{1}{2N_0} \left\{ \sqrt{D_b^2 + \Delta_c^2} - \sqrt{D_a^2 + \Delta_c^2} \right\} \quad (33)$$

These expressions are valid for all ratios of Δ_c , D_a , and D_b . When we assume $\Delta_c \gg D_a, D_b$, we find the somewhat simpler result (34).

$$p_{\mathbf{R}}(\infty) = \left\{ 1 + \frac{4\Delta_c^2}{D_b^2 - D_a^2} \ln \left(\frac{D_b}{D_a} \right) \right\}^{-1} \quad (34)$$

Only in Equation (34) have we made use of $\Delta_c \gg D_a, D_b$, thus that $p_{\mathbf{R}}(\infty)$ remains small. *Again $p_{\mathbf{R}}$ does not oscillate as $t \rightarrow \infty$* (neglecting terms of the order $1/N$). Under these conditions an initial optical activity due to the condition $p_{\mathbf{L}}(0) = 1$ will relax to a somewhat smaller than initial but still large value. In contrast to the result of Section 4.1, one cannot be sure that this result will be applicable in practice, neglecting collisional and radiative effects. This will only be true, if for some molecule the ΔE_{PV} is quite large. In this case we could learn about ΔE_{PV} from the kinetics of racemization. Fundamentally similar results are also obtained for the physically less likely case that ΔE_{PV} varies strongly with the rovibrational quantum state. Assuming for instance $F(\Delta)$ and $G(D)$ to be constant in the interval $-\Delta_m \leq \Delta \leq +\Delta_m$ and $-D_m \leq D \leq +D_m$ and zero outside, one finds a relaxed ($t \rightarrow \infty$) population ($\Delta_m \gg D_m$) [Eq. (35)].

$$p_{\mathbf{R}}(\infty) = \left(\frac{\pi D_m}{8\Delta_m} \right) + \frac{1}{4} \left[1 - \left(\frac{D_m^2 + \Delta_m^2}{D_m \Delta_m} \right) \arctan \left(\frac{D_m}{\Delta_m} \right) \right] \quad (35)$$

Separate forward and backward fluxes cannot be defined in any of these cases. Probability "appears" through tunnel-

ing across the boundary. Nevertheless, if one defines forward and backward rate coefficients in a kinetic relaxation scheme [Eq. (b) in Section 3.1], which is approximately possible, the rate coefficients depend upon the initial state and do not satisfy the detailed balance relationship Equations (3) or (11). This is an unusual situation in kinetics, which has, however, been encountered before.^[77]

4.3. Very Large Densities of States: Pauli Equation for Racemization

For polyatomic molecules with more than 10 to 20 heavy atoms one can estimate with approximations such as Eq. (9) or by more accurate calculations^[76] that the density of rovibronic states even at modest energies ($\approx 50 \text{ kJ mol}^{-1}$) quickly becomes sufficiently large that (36) holds true.

$$\delta = \varrho^{-1} \ll \Delta E_{\pm}, (\Delta E_{\text{PV}}) \quad (36)$$

The hamiltonian matrix can no longer be brought into the block diagonal structure as in Equation (18) and, in general, any level of the **R** isomer will be coupled to many levels of the **L** isomer and vice versa. A finite matrix expansion of Equations (13)–(16) would then require matrices of the order of at least many times $\Delta E_{\pm} \varrho$ or $\Delta E_{\text{PV}} \varrho$, which will be large numbers. Making use of statistical assumptions that have been discussed in detail elsewhere^[77,79] one can derive a Pauli equation for the specific rate coefficients $k_{\text{RL}}^{\text{micro}}(E)$ and $k_{\text{LR}}^{\text{micro}}(E)$ as a function of excitation energy E [Eqs. (37) and (38)].

$$k_{\text{RL}}^{\text{micro}}(E) = 2\pi \langle D_{\text{RL}}^2 \rangle \varrho_{\text{R}}^{\omega} \quad (37)$$

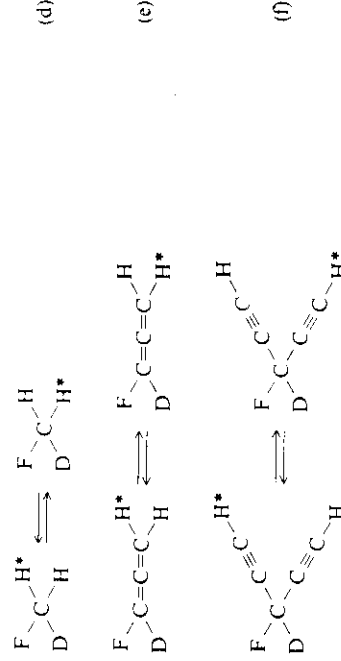
$$k_{\text{LR}}^{\text{micro}}(E) = 2\pi \langle D_{\text{LR}}^2 \rangle \varrho_{\text{L}}^{\omega} \quad (38)$$

$\langle D_{\text{LR}}^2 \rangle$ is the mean square "tunneling" coupling between all quantum states of **R** and **L** isomers at energy E in an interval ΔE which is large enough to render the average meaningful (D_{RL} cannot be calculated directly by a two-level tunneling model). The $\varrho^{\omega} = h\varrho/2\pi$ are the densities of states in circular frequency units. In contrast to the results of Section 4.2, Equations (37) and (38) satisfy the detailed balance relationship in Equations (11) and (12). The optical activity will relax to zero (practically) with a relaxation time $\tau_{\text{R}} = 1/(k_{\text{RL}} + k_{\text{LR}})$. Again, it will not oscillate. The density of states ϱ that has to be considered in the inequality (36) is not the full density of states but rather only the density of those states that are effectively coupled (by matrix elements of the order $\sqrt{\langle D_{\text{LR}}^2 \rangle}$). The transition between the situations in Sections 4.1 and 4.2 ("cases C" of Ref. [77]) and the Pauli equation ("case B" of Ref. [77]) will happen at values $\varrho^{-1} \approx \Delta E_{\pm}$. From studying this transition experimentally one would thus learn about the coupling dynamics between the **R** and **L** isomers in real polyatomic molecules, beyond the two-level approximation. The experiment would simply use the rapid increase of both ϱ and ΔE_{\pm} with excitation energy. The infrared laser chemistry of racemization has recently been discussed in this context.^[77b]

4.4. Dynamic Chirality and the Possible Existence of Chiral Methane

The common description of chiral molecules is based upon a Born-Oppenheimer potential with a double well and a barrier (such as in Fig. 1), which separates the two enantiomers. Racemization may occur in this description either by quantum tunneling through the barrier or by a quasiclassical barrier crossing above the barrier. We have stressed before that this description is unnecessary. This may appear obvious, because an observed *phenomenon* such as chirality, cannot depend on some arbitrary approximation that we use for its description. Atomic chirality is known to occur where this description would be meaningless.^[41] It may be useful to complement these general observations with specific *molecular* examples of *dynamical chirality* beyond Born-Oppenheimer potentials.

Work by Mecke^[80] and more recently by Child and Lawton^[81] and others^[82] suggests that high overtone excitation of high frequency modes in molecules with equivalent X–H modes may lead to long-lived localized vibrational excitations ("local modes"), in the following examples marked by asterisks.



Molecules with such localized vibrational excitations are chiral. The coupling including racemization is entirely vibrational (rotational) and unrelated to any electronic potential barriers. Although the lifetimes for localized states have probably been overestimated in early work,^[81,83] current evidence suggests that whereas the racemization (d) may occur on the subpicosecond time scale, the racemization (e) should be slower and in the case of acetylenic CH (or also alcoholic OH) stretching modes may exceed many picoseconds.^[84] Such dynamic chirality could be studied by time resolved vibrational spectroscopy.^[85] No direct experimental evidence has yet been presented, but one can be fairly certain from indirect evidence that the phenomenon exists.

Another kind of dynamic chirality has recently been proposed on the basis of localized *electronic* carbonyl excitation in an adamantanone.^[86] The chirality and its lifetime has not yet been established experimentally. Optical activity in vibrationally twisted allene has been discussed as well.^[88] One should realize that also *rotation* may induce a dynamic asymmetry or chirality, for example by centrifugal distortion (for magnetic effects see Ref. [89]).

A particularly interesting case of dynamic chirality is methane, by tradition the prototype of an achiral, highly symmetric, tetrahedral molecule.^[20] We shall discuss the consequences of parity violation and methane inversion from the present point of view. Figure 2 gives a rotational

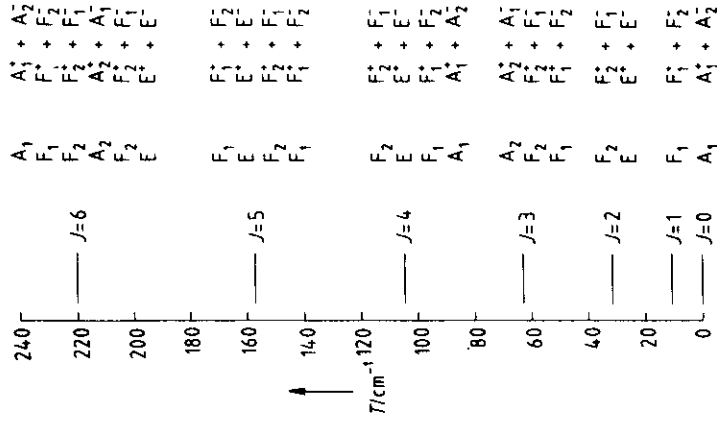


Fig. 2. Rotational energy level scheme for methane with symmetry assignments as explained in the text (after Ref. [100]). $T =$ term value $= E/(hc)$ (for nomenclature cf. also Ref. [73]).

energy level scheme for methane. The zero order spherical top levels shown at the left-hand side are split by centrifugal distortion into sublevels, classified in the point group species (A_1, A_2, E, F_1, F_2) as shown in the middle. These strongly J -dependent splittings are large, of the order of 0.1 cm^{-1} here, and can be much larger. Each of these levels is further split by a very small amount into a sublevel of positive and negative parity (+, -) as indicated by the molecular symmetry group species notation on the right-hand side.^[74, 75] (In Ref. [99] a different nomenclature has been used. According to the authors involved, the current nomenclature from Ref. [75] should be preferred.) It turns out that for CH_4 only the A_2^\pm (combining with nuclear spin $I = 2$), the F_1^\pm (combining with nuclear spin $I = 1$) and the E^\pm (combining with nuclear spin $I = 0$) exist, because of the Pauli principle. Thus the $A_{1,2}$ and $F_{1,2}$ levels in T_D have all well defined parity (either + or -) and there is no inversion splitting for these. However, the E^\pm pair does occur. Whereas in an asymmetrically substituted molecule with a high barrier the \pm splitting due to tunneling must be very small for symmetry reasons, in a symmetrical molecule such as methane there are further contributions to this splitting, which are still very small but which are potentially much larger than the tunneling splitting. According to all current quantum chemical evidence the inversion splitting must be very small in methane.^[97] There have also been experimental investigations on this question.^[98, 99]

Nevertheless, for special dynamical reasons, or by using the influence of external fields as in atoms,^[40, 41] the splitting may be made very small for some E^+, E^- level pair, so that $\Delta E_{\pm} \ll \Delta E_{\text{PV}}$. In this case ΔE_{PV} will generate new levels ϱ and λ (see Appendix), which have no well defined parity and are chiral: The probability density distribution $|\Psi_{\lambda, \varrho}(x, y, z)|^2$ for the four protons around the carbon nucleus will be asymmet-

ric. This effect can be tested by a spectroscopic experiment (in principle also by diffraction methods, but accuracy will be too low there). It leads in any case to a fundamental revision of the stereochemical concepts introduced by *van't Hoff* and *Le Bel* some 100 years ago.^[20]

4.5. Effects of Collisional and Radiative Processes

A complete treatment of collisional and radiative processes in a complex multilevel problem is beyond the scope of this article. However, we shall provide a phenomenological discussion of the effects expected in relation to the kinetic schemes in Sections 4.1. to 4.3. These complement the two-level treatment of collisions given by *Harris* and *Stodolsky*.^[44]

Collisional and radiative effects can be introduced in general in a *reduced* density matrix equation of motion by adding non-Hamiltonian terms (cf. Eq. (16)). They can also be simulated approximately by phenomenologically adding contributions from a continuous spectrum to the molecular hamiltonian (Eqs. (13) and (18)), for instance in the form of complex energies $E_k - i\Gamma_k/2$ with a width Γ_k . The effect on kinetic schemes as described in Sections 4.1 to 4.3 is known. The width has the effect of changing the density of states from a Dirac δ -distribution to a more continuous function.^[77] Then, by connecting the blocks of the effective hamiltonian instead of the relaxation [Eqs. (26), (28) or (32)] one has a transition to the Pauli equation rate coefficients (37) and (38). This changes somewhat the relaxation rate, but always leads to *complete racemization* at $t \rightarrow \infty$. In this sense collisions and spontaneous and thermal radiative processes *promote* racemization. This is somewhat in contrast to the result of *Harris* and *Stodolsky*,^[44] not because their theoretical result would be subject to doubt, but because here we consider a complex multilevel problem at finite energy, whereas their result refers to the $T \rightarrow 0, E \rightarrow 0$ limit of a pure two-level problem. Of course, the present qualitative predictions can be tested by experiments similar to those we have proposed in Section 3. There is no evidence available on chiral molecules. However, in a dynamically very similar case of IR-multiphoton excitation, collisions were, indeed, found to enhance the corresponding equilibration process by the mechanism discussed above, which has also been established experimentally.^[87]

5. Conclusions

We have demonstrated that different current hypotheses about the physical-chemical structure of chiral molecules lead to experimentally distinguishable consequences. Possible experiments using spectroscopic probes of molecular quantum state structure or probing the kinetics of racemization have been proposed. Although difficult and expensive (on the chemical, not particle physics scale) they would seem worthwhile in order to experimentally settle the questions posed.

It has been known to chemists and biologists for 140 years that chiral molecules carry a message for living beings: Chirality determines the fragrance of fruits, it can make all the

difference between bitter and sweet and it may distinguish healthy drug from deadly poison.¹¹⁰¹¹ Chiral molecules recognize each other not just as key and lock but as hand and glove. It is also believed by many that chiral compounds in nature are messengers of the evolution of living beings.

It seems to be much less well known that molecular chirality may carry an as yet hidden message on the subtle physical forces governing molecular structure and dynamics and, perhaps, following the motto by *Pasteur*, on the structure of our universe.

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Appendix: Some equations for the matrix representations of the two level problem with near degeneracies.

The hamiltonian matrix has the form (A 1). The eigenvalues for a hermitian operator H (A 2) follow from (A 3).

$$H = \begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \quad (\text{A } 1)$$

$$H_{12} H_{21} = H_{12} H_{12}^* = |H_{12}|^2 \quad (\text{A } 2)$$

$$E_{1,2} = \frac{H_{11} + H_{22}}{2} \pm \frac{1}{2} [(H_{11} - H_{22})^2 + 4|H_{12}|^2]^{1/2} \quad (\text{A } 3)$$

If we work in the basis χ_{\pm} of states of well defined parity and take ΔE_{PV} as perturbation one may identify (with real H_{12} and positive ΔE_{\pm}) the expressions (A 4) and (A 5).

$$\Delta E_{PV} = 2 H_{12} \quad (\text{A } 4)$$

$$H_{11} = -\Delta E_{\pm}/2 = -H_{22} \quad (\text{A } 5)$$

If we work in the basis of "left" and "right" handed states λ and ϱ , one has (positive ΔE_{PV}) the equations (A 6) and (A 7).

$$H'_{11} = -\Delta E_{PV}/2 = -H'_{22} \quad (\text{A } 6)$$

$$\Delta E_{\pm} = 2 H'_{12} \quad (\text{A } 7)$$

The eigenvalues with respect to the average energy $(E_1 + E_2)/2 = \langle E \rangle \equiv 0$ are obviously the same (ΔE_{\pm} and ΔE_{PV} are defined real, positive) [(A 8)]. It is immaterial, whether ΔE_{PV} (Ref. [50]) or the tunneling ΔE_{\pm} (Section 4) is introduced as "perturbation".

$$E_{1,2} = \langle E \rangle \pm \frac{1}{2} (\Delta E_{\pm}^2 + \Delta E_{PV}^2)^{1/2} \quad (\text{A } 8)$$

Eigenvectors for the example of basis χ are given by (A 9) where x and y are defined via S [Eq. (A 10)] according to (A 11) and (A 12).

$$C = \begin{pmatrix} x & y \\ -y & x \end{pmatrix} \quad (\text{A } 9)$$

$$S = (\Delta E_{\pm}^2 + \Delta E_{PV}^2)^{1/2} \quad (\text{A } 10)$$

$$x^2 = \frac{S + \Delta E_{\pm}}{2 S} \quad (\text{A } 11)$$

$$y^2 = \frac{S - \Delta E_{\pm}}{2 S} \quad (\text{A } 12)$$

The signs of the roots $\sqrt{x^2}$ and $\sqrt{y^2}$ can be taken in various combinations respecting $C^T C = I$ (S is defined positive). One has by convention $E_1 < E_2$ and $H_{11} < H_{22}$. Some sign combinations in Ref. [50] were inconsistent with the correct figure ($E_{\lambda} < E_{\varrho}$). Figure 3 represents the situation ($x = y = 1/\sqrt{2}$ [Eq. (A 13)–(A 16)].

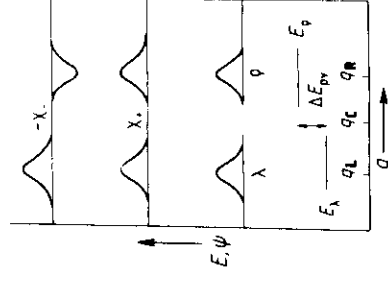


Fig. 3. Scheme for wave functions in a nearly degenerate situation ($\Delta E_{\pm} \approx 0$) in a chiral molecule (see text).

$$\lambda = \frac{1}{\sqrt{2}} (\chi_+ - \chi_-) \quad (\text{A } 13)$$

$$\varrho = \frac{1}{\sqrt{2}} (\chi_+ + \chi_-) \quad (\text{A } 14)$$

$$\lambda_+ = \frac{1}{\sqrt{2}} (\lambda + \varrho) \quad (\text{A } 15)$$

$$-\lambda_- = \frac{1}{\sqrt{2}} (\lambda + \varrho) \quad (\text{A } 16)$$

According to the superposition principle (if valid) these can always be generated by one of the methods of Section 3. The time evolution results from Equation (A 17) giving Equation (22) for $P_{RR} = P_R$, for example.

$$U = C \begin{pmatrix} \exp(-i E_1 t/\hbar) & 0 \\ 0 & \exp(-i E_2 t/\hbar) \end{pmatrix} C^T \quad (\text{A } 17)$$

The density matrix with the elements $P_{ij} = \langle c_i c_j^* \rangle$ ($\langle \rangle =$ average over an appropriate ensemble) has the form (A 18) in the λ -Q basis and the form (A 19) in the χ -s basis.

$$\begin{pmatrix} P_{RR} & P_{RL} \\ P_{LR} & P_{LL} \end{pmatrix} = P^{\lambda, e} \quad (\text{A } 18)$$

$$\begin{pmatrix} P_{++} & P_{+-} \\ P_{-+} & P_{--} \end{pmatrix} = P^{\chi, s} \quad (\text{A } 19)$$

For the degenerate system (or nearly degenerate system) at any temperature with $kT \gg S$ (A 10) Equation (A 20) holds.

$$P^{\lambda, e} = P^{\chi, s} = \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & \frac{1}{2} \end{pmatrix} \quad (\text{A } 20)$$

P is invariant under the basis transformation (as any other constant diagonal matrix), also in the many level case, if H is block diagonal as in Equation (18). A racemic mixture of R and L is identical to a mixture of $+$ and $-$ in terms of any observable ensemble property. A common model for P , simplified for the degenerate case, considered as a reduced density matrix of the molecule interacting by collisions or otherwise with a thermal bath gives the expressions (A 21) and (A 22), from which the relationships (A 24) and (A 25) can be derived for the relaxation times given here by τ_1 and τ_2 with the basis transformation (A 23).

$$(P_{11} - P_{22}) = (P_{11}^0 - P_{22}^0) \exp(-t/\tau_1) \quad (\text{A } 21)$$

$$P_{12} = P_{12}^0 \exp(-t/\tau_2) \quad (\text{A } 22)$$

$$P^{\chi, s} = C P^{\lambda, e} C^T \quad (\text{A } 23)$$

$$\tau_1^{\chi, s} = \tau_1^{\lambda, e} \quad (\text{A } 24)$$

$$\tau_2^{\chi, s} = \tau_2^{\lambda, e} \quad (\text{A } 25)$$

Here we have made use of the reality of P in the case of a degenerate model, because $E_{1,2}$ can be set to zero without loss of generality. To within this approximation the assignment of "phase" or "population" relaxation times τ_1 and τ_2 is arbitrary in the two level problem (cf. Section 3).

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On the measurement of *CP*-violating energy differences
in matter–antimatter enantiomers ☆

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On the measurement of CP -violating energy differences in matter-antimatter enantiomers \star

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Abstract

Experiments are outlined for measuring possible, hypothetical CP -violating energy differences arising in chiral molecules and their antimatter-molecule enantiomers. While at present not within the reach of current experimental techniques due to the difficulty of synthesizing and trapping antimatter-molecules, such experiments are feasible, in principle, not just as thought experiments. The experiments help to clarify some fundamental concepts of C , P , and T symmetry violations in molecular physics with connections both to elementary particle physics and cosmology. They would constitute potentially by far the most sensitive proposed test for CP symmetry violation.

1. Introduction

We have proposed realistic experiments to measure parity (P) violating energy differences ΔE_{p} between the two enantiomers of chiral molecules [1,2]. While such energy differences have been calculated [3-5], they have not yet been confirmed experimentally and thus remain hypothetical. Nevertheless, we have shown that experimental tests are within the reach of present day technology and long term efforts towards this goal are under way in our laboratory. The experiments would also help to clarify some fundamental issues of molecular chirality [6-11].

In Ref. [1] we briefly drew attention to the close connection to other aspects of C , P , and T violation in molecular physics (see below for nomenclature). Historically the position of theoreticians and philosophers has been (with notable exceptions [6]) to take certain symmetries as fundamental 'a priori' proper-

ties of nature [12-17]. The finding of parity violation [18] and subsequently CP violation [19] dealt a blow to such beliefs. It is interesting that theoretical withdrawal has been gradual, assuming for example, first CP symmetry once P violation had been proved [20], then, after finding CP symmetry violated, CPT symmetry [13-15].

In a recent lecture [21] we took, on speculative grounds, the opposite point of view, i.e. that one might start from the hypothesis of the violation of all fundamental symmetries in molecular physics, and in particular all *discrete* symmetries, as opposed to the *continuous* symmetries, which have a slightly different status. These symmetries may be summarized in terms of conservation laws and the invariance of the molecular Hamiltonian with respect to [21-24]:

- (i) any overall translation in space (continuous, related to momentum conservation)
- (ii) any translation in time (continuous, related to energy conservation)
- (iii) any rotation of all particle coordinates in space

\star Dedicated to Professor Dr. W. Lütke on the occasion of his 75th birthday.

(continuous, related to angular momentum conservation)

(iv) the reflection of all particle coordinates in the centre of mass (P or F^* , discrete, related to parity conservation)

(v) time reversal or the reversal of particle momenta and spins (T , discrete, related to the reversibility of molecular or more general classical and quantum mechanical motion)

(vi) any permutation of the indices of identical particles (nuclei and electrons, discrete, related to the generalized Pauli principle)

(vii) replacement of all particles by their antiparticles (discrete, related to 'charge conjugation', C , with change of the sign of the electric charges).

Usually, experiments on the fundamental, discrete symmetries have been carried out in the realm of elementary particle and high energy physics. As has been pointed out [1,2,21,25], molecular physics might be an interesting testing ground particularly in relation to the near-degeneracy provided by enantiomers of chiral molecules, which will render effects arising from certain small symmetry violations more easily visible.

Fig. 1 illustrates this situation [21]. A chiral molecule such as CHFClBr , alanine, or many others [2], including isotopomers such as CHDTH , can occur in its left-handed (L) or right-handed (R) form (we do not use any specific convention for nomencla-

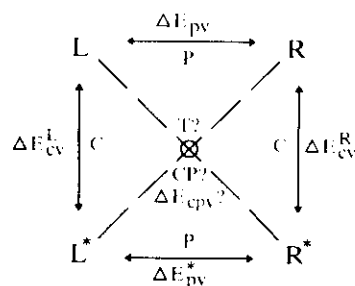


Fig. 1. Scheme connecting various optical isomers composed of matter (L , R) and antimatter (L^* , R^*) with the symmetries C , P , and T and their possible violations mentioned (see also text). Hypothetical energy differences are ΔE_{pv} and ΔE_{cpv} . The figure was given in Ref. [21], and a similar figure with different notation is given by Barron [28], who removed, however, the 'T' and the question marks which had originally been introduced to stress perfectly open current questions.

ture). With P symmetry these would be energetically exactly equivalent, transformed into each other by inversion (i.e. E^* or P). In fact, parity violation may perhaps introduce a small energy difference ΔE_{pv} , resulting in a nonequivalence of the two isomers or enantiomers, which are not any more simple mirror images of each other in this case. If the corresponding molecules are made of antimatter (indicated by an asterisk L^* and R^*), one has a similar hypothetical energy difference ΔE_{pv}^* due to parity violation. If there were no CP violation the two molecules L and R^* connected by CP would be exactly equivalent, energetically, and otherwise (consider a total angular momentum including spin and nuclear spin zero, for simplicity). In that case $\Delta E_{pv} = \Delta E_{cv}$, obviously. If, however, one found experimentally a small ΔE_{cpv} between L and R^* , this would imply CP violation in molecular physics. As we have discussed [25], under certain circumstances such an experiment might also provide a most stringent test of the particle-antiparticle mass equivalence, as L and R^* may be considered as the relevant particle-antiparticle pair states, and hence a test of CPT symmetry connecting particle and antiparticle masses [26–28]. Current tests of this mass equivalence are comparatively crude, particularly with baryons [27].

In principle, the measurement of energy differences in the scheme of Fig. 1 is straightforward. For the L - R pair, one could measure the heat of combustion [6], to give achiral common products; for the L - R^* pair one might measure the absolute mass or complete annihilation energies ('heats of annihilation') with the respective achiral particle combinations or certain combinations of chiral pairs. In practice, this meets with difficulty, as the expected energy differences, if any, are so small that no such experiment has sufficient precision to hope for success. For measuring ΔE_{pv} in ordinary molecules one may carry out simultaneous experiments on L - R pairs, even involving superpositions of L and R states, and thereby obtain perhaps the precision needed for measuring extremely small ΔE_{pv} , of the order of 10^{-14} J mol $^{-1}$ [1–5]. For a pair such as L - R^* the difficulty arises that antimatter-molecules cannot be prepared in the laboratory to date, and even if they were, care would have to be taken to avoid all contact of the chiral antimatter-molecules with ordinary matter. For this reason the following considerations concern experi-

ments that are *not* currently feasible and therefore were not included in the previous written report of our lectures, which had strict length limitations [21]. On the other hand, recent discussions [28] of our proposal [21] render a more detailed description useful, as it may help to clarify some of the basic concepts. Also it cannot be excluded that, in the future, chiral antimatter-molecules may become accessible and with such a long term view the ideas may be useful.

One concept in question concerns the meaning of 'exact' enantiomeric relationship. Barron has argued [28,29] that even if the exact mirror image relation between L and R enantiomers is lost, because of parity violation, one still would retain such a relation for L and R^* (or L^* and R) ' CP -enantiomers', for which he coined the term 'true enantiomers'. As pointed out in Ref. [21], if one allows for ΔE_{cpv} this 'exact' enantiomeric relation is lost for the L - R^* pairs, as it is lost for the L - R pair due to parity violation. As far as etymology is concerned we note that enantiomer comes from $\epsilon\nu\alpha\nu\tau\iota\omicron\varsigma$ (Greek, meaning 'opposite') and $\mu\epsilon\gamma\omicron\varsigma$ (meaning 'part') which leaves the importance of 'exact' mirror equivalence rather open.

An aim of the present Letter is to demonstrate that real experiments are feasible, in principle, which would allow the measurement of CP -violating energy differences in chiral molecule-antimatter molecule pairs. In our proposals on the measurement of ΔE_{pv} we were able to provide the necessary estimates of both experimental observables and parasitic effects and could thus demonstrate that the experiments are actually feasible in practice, even if rather difficult. To avoid misunderstandings, we stress that our considerations on the measurement of ΔE_{cpv} do *not* attempt any analysis of experimental complications that obviously arise in numerous ways, as the direct experiments discussed below are not planned to be feasible in the near future, i.e. the present decade or so. Therefore we do not make any effort to phrase the description in a realistic experimental setting but stay at the level of experimental principles. In the Section 3, we shall briefly mention alternative, indirect routes towards the same goal.

2. The principles of the experiments

We shall consider the question of the four isomer ground state energies in Fig. 1 as an entirely empirical problem. Fig. 2 shows these energies denoted with the 'isomer' labels L , L^* , R^* and R , together with some selected excited states on the respective ladders, which we shall discuss below. The first, obvious way to place the four 'isomer' energies on an absolute scale would be to measure their mass by some mass spectrometric technique and obtain the energy difference from the mass differences. For instance, proton-antiproton masses have been compared (and found to be equal) with an uncertainty of $\Delta m/m \approx 4 \times 10^{-8}$ in cyclotron

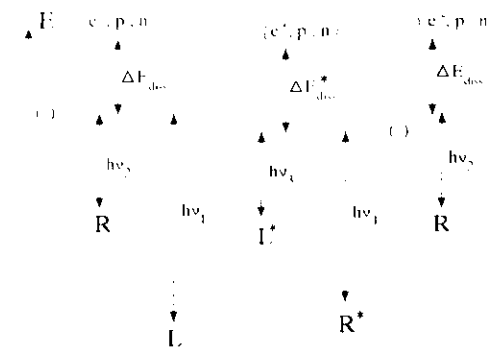


Fig. 2. Energy level scheme for explaining possible measurements of energy differences of the L , R , L^* , R^* isomers in Fig. 1. The energies given can be read (schematically) as absolute energies or masses of the relevant particles at rest in the quantum state given (ground state if not otherwise indicated). The set of particles $\{e^-, p, n\}$ is meant to contain the relevant numbers of electrons, protons and neutrons corresponding to the chiral molecules L and R (obviously the numbers are the same) and similarly for the antimolecules L^* and R^* (with antiparticles e^+ , \bar{p} , \bar{n}). We note that pairs (L^* and L) and (R^* and R) can be referred to the same set of elementary particles $\{e^+, p, n, e^-, p, n\}$ at complete dissociation. The molecules (L^* , L , R^* , R) are stabilized with respect to the free particles by an energy amount ΔE corresponding to a mass difference Δmc^2 as shown in the scheme. One could also introduce as intermediate levels the bound nuclei in their respective ground states. The various energy differences are not at all drawn to scale, the differences between L , R , L^* , R^* ground state levels being exaggerated by more than about 20 orders of magnitude, for the purpose of illustration, with respect to the other energies. The ground state levels do not have well defined parity, whereas the intermediate spectroscopic levels indicated do (for instance negative parity ' $-$ ' as indicated. See also discussion in the text).

resonance experiments, which seems to be the most accurate result to date for baryonic matter [27], earlier experiments having achieved $\Delta m/m$ of the order of 10^{-5} . In the ‘mesonic’ K-meson experiments one has currently $\Delta m/m \approx 10^{-18}$ [34]. If one accepts $\Delta m/m \approx 10^{-10}$ for the current mass spectroscopic technology in measuring L, R* masses this would correspond to about 1.5×10^{-18} J (for $m \approx 100$ u) or 1000 kJ mol⁻¹ which is far above the expected range of energy differences (perhaps 10^{-15} J mol⁻¹). It is difficult to see how improvements of mass spectrometry could bridge such a gap.

The same kind of limitation applies if we wish to measure masses by mass spectrometry of the elementary particles e⁻, p, n and e⁺, p̄, n̄ at complete dissociation (instead of p, n, the corresponding nuclei would do as well) and relate the energies of L, L*, R*, R to this limit by measuring a chain of spectroscopic energies by high-resolution techniques (ΔE_{diss} , ΔE_{diss}^* , $h\nu_i$) as outlined in Fig. 2. One must note that the energies of the set of free particles at rest {e, p, n} and {e⁺, p̄, n̄} cannot be assumed to be the same, in general, as this would anticipate partly the result to be demonstrated. Because of this lack of accuracy, we shall not further discuss the direct mass spectroscopic techniques, even though they are in principle able to solve the problem.

Rather we shall analyze an experiment aimed directly at energy differences as shown in Fig. 2. In this figure we have drawn an excited (electronic or vibrational) level of well-defined parity (– for example) above each ground level. The spectroscopic situations leading to such a scheme have previously been discussed in considerable detail [1,2]. These excited levels of (almost) well-defined parity are accessible by electric dipole transitions from both ground states (R, L) or (L*, R*). Therefore we have drawn the corresponding levels jointly for these pairs. Furthermore in a second step one may determine the dissociation energies ΔE_{diss} (or ΔE_{diss}^* , not necessarily the same) leading to elementary particles, or at least nuclei and electrons and the respective antiparticles.

Consider now pairs of molecules L + L* and R + R*, where each of the four (L, L*, R, R*) is supposed to be investigated spectroscopically in an individual ultrahigh vacuum trap (or in a molecular beam of well-defined velocity in vacuum). This prevents annihi-

lation. We may establish an energy balance for the sum of the energies $\{E_L + E_{L^*}\}$ and $\{E_R + E_{R^*}\}$, where we note that with CP symmetry these would be the same (see Fig. 1). Here, we allow for a difference, noting, however, that $\{L + L^*\}$ and $\{R + R^*\}$ dissociate to identical sets of elementary particles, namely {e⁻, p, n, e⁺, p̄, n̄} (we do not give in our notation the numbers of particles, which depend upon the composition of the molecules). This allows us to place $\{E_L + E_{L^*}\}$ and $\{E_R + E_{R^*}\}$ on the same energy scale using only measurable quantities as shown in Fig. 2,

$$h\nu_1 + h\nu_3 + \Delta E_{\text{diss}} + \Delta E_{\text{diss}}^* = -\{E_L + E_{L^*}\}, \quad (1)$$

$$h\nu_2 + h\nu_4 + \Delta E_{\text{diss}} + \Delta E_{\text{diss}}^* = -\{E_R + E_{R^*}\}. \quad (2)$$

By considering such sums of energies, we circumvent the inaccurate determination of absolute masses. We use the fact that $\{L + L^*\}$ and $\{R + R^*\}$ dissociate into the same set of particles and antiparticles (and thus to identical achiral product mass and energy levels) and furthermore that the pairs $\{L + L^*\}$ and $\{R + R^*\}$ are connected to each other by the CP operation (see Fig. 1). We note now that Eqs. (1) and (2) contain as one part ΔE_{diss} and ΔE_{diss}^* , which are difficult to measure and therefore relatively inaccurate (but much more accurate than the 1000 kJ mol⁻¹ mentioned above), and a part which is accurate, namely the $h\nu_i$, limited only by the techniques of ultrahigh resolution spectroscopy. Taking the difference of (1) and (2) we remove the inaccurate part

$$\begin{aligned} (h\nu_2 + h\nu_4) - (h\nu_1 + h\nu_3) \\ = \{E_L + E_{L^*}\} - \{E_R + E_{R^*}\}. \end{aligned} \quad (3)$$

On the left-hand side we have only accurately measurable quantities. Obviously, with CP symmetry, Eq. (3) results in zero energy difference. However, with CP violation one finds, as illustrated in more detail in the scheme of Fig. 3,

$$(h\nu_3 + h\nu_4) - (h\nu_1 + h\nu_2) = \Delta E_{\text{cpv}}^* - \Delta E_{\text{cpv}} \quad (4)$$

and

$$\Delta E_{\text{cpv}} - \Delta E_{\text{cpv}}^* = \Delta E_{\text{cpv}}^{\text{R}^* \text{L}} + \Delta E_{\text{cpv}}^{\text{L}^* \text{R}}. \quad (5)$$

The right-hand side of Eq. (5) gives appropriate sums of ΔE_{cpv} , which can thus be determined in this way to within the usual spectroscopic accuracy (say, perhaps 10^{-4} J mol⁻¹ for high-resolution spectroscopy of the ν_i).

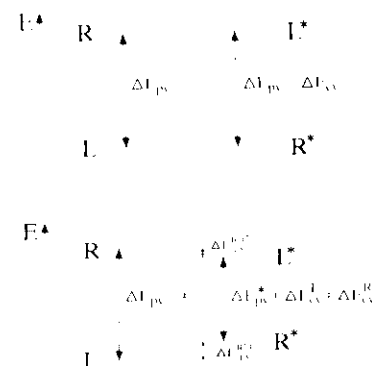


Fig. 3. Simplified energy level scheme for ground state energies of the four isomers in Fig. 1, defining various energies and energy differences as indicated. The upper part is with CP symmetry, the lower part with CP symmetry violation. See also discussion in the text.

However, one may gain another ten orders of magnitude by noting that ΔE_{cpv} and ΔE_{cpv}^* can be determined much more accurately, in principle, by performing the superposition experiment proposed in Ref. [1] both on a pair (L, R) (giving ΔE_{cpv}) and on a pair (I*, R*) (giving ΔE_{cpv}^*). In this experiment we make use of the special degeneracy existing in this dynamical system and an accuracy of perhaps 10^{-14} J mol⁻¹ or even better might be achieved for ΔE_{cpv} . If we assume that there is no considerable cancellation (i.e. $\Delta E_{\text{cpv}}^{\text{R}^* \text{L}}$ and $\Delta E_{\text{cpv}}^{\text{L}^* \text{R}}$ of the same magnitude but different sign), this amounts to an accuracy of about 10^{-14} J mol⁻¹ achievable for energy differences arising from CP violation in this system. With some cancellation, the effects would be reduced by the appropriate order of magnitude. In the ‘favourable’ case (i.e. $\Delta E_{\text{cpv}}^{\text{R}^* \text{L}} \approx \Delta E_{\text{cpv}}^{\text{L}^* \text{R}}$) one finds a possible accuracy, given as uncertainty in terms of a hypothetically measured effect ΔE

$$\frac{\Delta E}{E} = \frac{\Delta m}{m} \approx \frac{10^{-14} \text{ J mol}^{-1}}{10^{+16} \text{ J mol}^{-1}} \approx 10^{-30}. \quad (6)$$

This is about 20 orders of magnitude better than the best current results for baryonic matter [27] and still 10 orders of magnitude better than the current K-meson results [34]. One might argue that a more proper scale for the sensitivity estimate would be obtained by using the total binding energy as E in the denomi-

nator, resulting in a sensitivity of about 10^{-20} instead of Eq. (6). This still would be somewhat better than the best bounds currently available, but if an energy ΔE in Eq. (6) were actually found, comparison with the total energy (mass) seems appropriate to us. Further evidence exists for leptonic matter (from positronium and myonium systems, again of much lower accuracy). Most recent proposals (still somewhat far from realization) on antihydrogen spectroscopy claim potentially attainable accuracies similar to the K-meson results (i.e. $\Delta m/m \approx 10^{-18}$), where it was also pointed out that the high accuracy achieved in analysis of the K-meson system is model-dependent in contrast to the still hypothetical antihydrogen spectroscopy [34]. We should also draw attention to the extensive search for neutron and other atomic electric dipole moments, related to CP violation in atomic physics. While high precision can be achieved in such experiments it is not easy to establish a direct link to the mass differences discussed here, which really concern a somewhat different matter. We refer to a recent review on electric dipole moments [35].

Therefore our approach using chiral molecules is interesting, although like all the experiments discussed in Section 3 it depends upon being able to prepare molecules (even chiral) in their ground state composed of antimatter. While antiprotons and the like are relatively easily prepared in accelerators and even stored for long times, the prospects for synthesizing molecules starting from such material do not currently look good. Nevertheless, the present section shows that it is possible to devise experiments which could measure CP-violating energy differences, if any, of about the order of magnitude that might be expected in the most favourable cases in chiral molecules. The ultimate accuracy in defining all energy differences in Fig. 3 would be achieved by combining the superposition experiments for ΔE_{cpv} and ΔE_{cpv}^* with a hypothetical coherent superposition of the $\{L^* + R^*\}$ pair with the $\{L + R\}$ pair involving possibilities for baryon and lepton nonconservation. Since both pairs are coupled to non-identical dissociative states this would be possible only, in principle, by coherent particle-antiparticle pair production with subsequent radiative transitions. The time evolution in the superposition state would be governed by the energy difference

$$\Delta E = (E_L + E_R) - (E_{L^*} + E_{R^*})$$

$$= \Delta E_{pv} - \Delta E_{pv}^* - 2\Delta E_{cpv}^{R^*L^*} \quad (7)$$

in analogy with our proposal for measuring ΔE_{pv} and ΔE_{pv}^* . It is difficult to see how such a pair creation experiment could be carried out accurately so this experiment is restricted to conceptual questions only. Other schemes are possible as well, perhaps with better accuracy, and there is no reason to reject such considerations as futile.

3. Discussion

The level scheme with four different ground state energies contains three significant energy differences, of which two could be measured with high accuracy by the schemes outlined, one only with low accuracy. As we know nothing about the outcome, we can only hope that the dynamical situation of extremely close degeneracy somehow would render the effects of weak symmetry violations visible, particularly so if the dynamics of parity violation is linked in some way to CP violation. In order to prevent possible misunderstandings we should stress that, of course, a calculation of ΔE_{pv}^* with the theories currently used for ΔE_{pv} [3–5] would give $\Delta E_{pv} = \Delta E_{pv}^*$ because they have a CP (and CPT) invariant Hamiltonian. We are discussing effects *beyond* such current theories.

If the outcome of one of the experiments is positive, either measuring directly $\Delta E_{cpv} \neq 0$ or finding in Eqs. (4) and (5) a nonzero result, this proves CP violation in chiral molecule–antimatter molecule pairs. We note furthermore that CP symmetry also implies that ν_2 and ν_3 on the one hand and ν_1 and ν_4 on the other (Fig. 2) must individually be the same, because the spectra of CP isomers would be degenerate (or else, individual CP isomer levels would not correspond to eigenfunctions of the CP invariant Hamiltonian). Thus, if one found a difference between ν_2 and ν_3 (or ν_1 and ν_4) this would also imply CP violation in these chiral molecules. This conclusion is in agreement with our earlier discussion [21] which remains valid as an acceptable speculation. We did, in particular, not exclude CPT violation in con-

junction with the observable ΔE_{cpv} , rather we stressed the possibility of violating *all* discrete symmetries. Current discussion of CP violations in K^0 meson experiments, for instance CPLEAR [30], allow explicitly for CPT -violating terms, although these have not yet been measured.

We have in Section 2 compared possible measurements of hypothetical ΔE_{cpv} in chiral molecules to measurements of hypothetical proton–antiproton mass differences or generally baryonic matter–antimatter mass differences, which are well known to constitute tests of CPT symmetry [25–28]. Indeed, tests for ΔE_{cpv} in chiral molecules under appropriate conditions can easily be seen to be equivalent to particle–antiparticle mass difference tests. To our knowledge, the first proposal to use the particular properties of the chiral molecules in the scheme of Fig. 1 for such tests along the lines of Section 2 was presented in Ref. [25]. A somewhat simplified reasoning containing the basic physics can be provided briefly, following [26]: If φ_m is an eigenfunction of \mathbf{H} describing a particle at rest with energy mc^2 then, if (CPT) commutes with \mathbf{H} , we find that $(CPT)\varphi_m$ describes the antiparticle with the same energy mc^2

$$\mathbf{H}(CPT)\varphi_m = mc^2(CPT)\varphi_m. \quad (8)$$

Now, since for a chiral molecule at rest with zero angular momentum (and spin) \mathbf{T} leaves the state unchanged (we could choose a real wavefunction) (CP) amounts to the same as (CPT) in that case, i.e. $(CPT)\varphi_m$ describes the CP isomer with the same energy mc^2 . If the degeneracy of the CP isomer ground level doublet or quadruplet were lifted, they may no longer be eigenstates of \mathbf{H} , but some linear combinations would be. A much more general derivation has been given by Barron [28]. We shall not discuss possible restrictions on these derivations and accept the result as valid, at least for special cases.

We should mention some possible logical fallacies in the context of CPT and CP violation in chiral molecules. The first fallacy is to assume, for instance, that one might ‘demonstrate’ (by invoking CPT symmetry), that there is no CP -violating energy difference ΔE_{cpv} in the scheme of Fig. 1 and that therefore L and R^* (and L^* and R) have an exact mirror relationship. As we have discussed above and before [21], an experimentally established ΔE_{cpv} would reject any presupposed exact mirror relationship.

The second possible and perhaps more subtle logical fallacy arises from the following reasoning: All currently available *experimental evidence is consistent with CPT symmetry* in particle (and atomic and molecular) physics. Therefore one might be tempted to exclude ΔE_{cpv} on the grounds of available experimental evidence. However, to exclude ΔE_{cpv} it would be necessary to have *positive experimental evidence which is inconsistent with CPT violation* under any of the circumstances considered. The reader will see the logical difference between the emphasized statements. To our knowledge there is no positive evidence of the second kind available for the problem under consideration. Thus the question is open and must be resolved by experiments.

This simple point is often overlooked in a variety of contexts and we have discussed it in relation to the structure and dynamics of ‘ordinary’ chiral molecules, whose foundations are subject to serious open questions [2] which still need experimental answers, and in some didactic detail also in relation to time-reversal symmetry and irreversibility [11,31]. In the latter case it is often noted that all available evidence is consistent with macroscopic irreversibility arising from microscopically reversible laws by means of de facto symmetry breaking. This is the widely accepted explanation of the statistical mechanical foundations of the second law. However there is no positive evidence which would be inconsistent with de lege time asymmetry providing a basis for the second law on long time scales, perhaps not the only one. Thus the question remains open here as well.

This leads us to consider the link between time-reversal symmetry and CP symmetry. That there is such a link is theoretically obvious in the CPT theorem [13,14]. A quantitative relation would allow us, in principle, to derive information equivalent to ΔE_{cpv} by measuring just violation of time-reversal symmetry, including perhaps also parity violation, in ordinary (chiral) molecules, thus circumventing the need to synthesize R^* and L^* molecules. Unfortunately, as already pointed out [21], the qualitative CPT theorem is insufficient for that purpose, as it just provides a yes–no answer. If CPT symmetry is, indeed, violated, we do not know how to derive quantitatively a ΔE_{cpv} from a hypothetically measured de lege violation of time-reversal symmetry in some process. One can, however, imagine a future, quantitative theory

beyond the qualitative CPT theorem, which would provide such a relation. It is desirable now to develop quantitative alternative theoretical models (beyond the standard model), including CPT violation, which would provide quantitative predictions of ΔE_{cpv} and other effects which could be tested in the experiments proposed. Inclusion of CPT violation in a new theory implies substantially rebuilding the current edifice of relativistic quantum and particle theories.

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Molecular Infrared Spectra and Molecular Motion*

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Molecular Infrared Spectra and Molecular Motion*

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We review recent work from our group in Zürich concerning molecular rovibrational motion in relation to molecular infrared spectra. After discussing general aspects of the dynamics of quantum systems under coherent and incoherent infrared excitation, including quantitative strengths of IR-absorption, we introduce the topic with the simplest examples of harmonic oscillator motion. We then survey the quantum dynamics of coupled vibrations in polyatomic molecules. We stress the importance of symmetry as a governing feature in molecular dynamics and illustrate this with the example of various symmetry conservation laws in chiral molecules.

1. INTRODUCTION

We have in a previous review in this series of conferences summarized in some detail our general approach to derive short time molecular quantum dynamics from molecular spectra as well as some of the pertinent results on time scales of intramolecular vibrational redistribution (IVR) and related problems [1]. The present review is complementary to this earlier review. We shall stress some of the current aspects of the dynamics of quantum motion under coherent and incoherent infrared excitation. Indeed, recent work has allowed us a fresh look on quantum wavepacket dynamics under infrared excitation both for simple model systems such as the harmonic oscillator and for chromophore oscillators in real polyatomic molecules. After giving an exemplary discussion of the recent results, we shall conclude with some complements on our previous discussion of the role of symmetry in intramolecular dynamics, in particular also some fundamental aspects of the dynamics of chiral molecules in the light of recent discussions of our earlier article [1]. As we had given a rather extensive list of references in our review [1], we shall not duplicate these here, but rather restrict our attention only to references of immediate importance to the present paper. We do not intend here to provide a general review, but rather a review of work from our own group, of course in relation to that of others, where appropriate.

*Lecture presented at EUCMOS 22, Essen, on 16 September 1994 and dedicated to Kurt Dressler on the occasion of his 65th birthday

2. THE DYNAMICS OF COHERENT AND INCOHERENT INFRARED EXCITATION

We shall discuss in this section the basic concepts of coherent and incoherent excitation in two-level and many level systems in relation to some recent progress, but also in the historical context. Some importance will be attached to quantitative aspects of the molecule radiation interaction, including the relation of excitation rates and integrated band strengths for infrared chromophores.

2.1 Coherent excitation with monochromatic radiation in the two level and the many level systems

Coherent excitation in a two level system subject to a linearly polarized quasi-classical monochromatic radiation field in the radiofrequency range was discussed early on by Rabi [2]. While his solution in the rotating wave approximation is very widely known and cited, it seems to be much less widely known that an exact analytical solution even for this simple model problem is not available until today, except for very special combinations of parameters [3]. Prior to the arrival of laser radiation, the use of a quasiclassical electromagnetic wave for infrared excitation would also have been questionable (in contrast to the radiofrequency case). However, intense infrared laser radiation, indeed, behaves largely as a classical radiation field, very similar to radiofrequency radiation. Furthermore, on time scales, say, of micro- to nanoseconds which are short compared to spontaneous emission lifetimes in the millisecond range for the strongest transitions in the infrared, it is well justified to neglect spontaneous emission. In this sense the arrival of coherent infrared laser light sources has effectively extended the "classical" radiofrequency range into a similarly "classical" infrared (IR) radiation range. The possibilities of tunability and pulse control are, however, still much less adequate in the IR compared to radiofrequencies.

The electric field strengths for z-polarized monochromatic radiation with a beam propagating in y direction follows the equation:

$$E_z(y,t) = |E_0| \cos(\omega t + \eta - k_\omega y) \quad (1)$$

where $|E_0|$ is the amplitude, ω the angular frequency, k_ω the wavenumber and η the phase of the field ($\eta' = \eta - k_\omega y$). Introducing electric dipole (μ) coupling, matrix elements between molecular stationary states φ_k and φ_j (unit vector e_z in z-direction)

$$M_{kj}^z = \langle \varphi_k | \mu e_z | \varphi_j \rangle \quad (2)$$

$$V_{kj} = -M_{kj}^z \frac{2\pi}{\hbar} |E_0| \quad (3)$$

one finds the time dependent differential equation in matrix form [3,4]:

$$i \frac{\hbar}{2\pi} \frac{dU}{dt} = H(t) U \quad (4)$$

$$\frac{2\pi}{\hbar} H(t) = W + V \cos(\omega t + \eta') \quad (5)$$

Of course, a similar equation results for magnetic dipole coupling, with changed definition of V . W is the diagonal matrix of angular eigenfrequencies from the field free molecular hamiltonian matrix H_{mol}

$$W = 2\pi H_{mol}/\hbar \quad (6)$$

The formal solution of the time dependent Schrödinger equation

$$i \frac{\hbar}{2\pi} \frac{\partial \Psi(r,t)}{\partial t} = \hat{H} \Psi(r,t) \quad (7)$$

is given by the expansion

$$\Psi(r,t) = \sum_k b_k(t) \varphi_k(r) \quad (8)$$

r represents the collection of space and spin coordinates and $\varphi_k(r)$ the corresponding stationary state of the molecule. The vector of time dependent coefficients \mathbf{b} is obtained by means of the time evolution matrix U from the equation

$$\mathbf{b}(t) = U(t, t_0) \mathbf{b}(t_0) \quad (9)$$

U (formally from Eq. (4)) solves also the Heisenberg equation of motion for the matrix representation Q of some observable as well as the Liouville - von Neumann equation for the density matrix P

$$Q(t) = U^\dagger(t, t_0) Q(t_0) U(t, t_0) \quad (10)$$

$$P(t) = U(t, t_0) P(t_0) U^\dagger(t, t_0) \quad (11)$$

As mentioned above, analytical, closed expressions are not available in general, and we shall discuss some useful current numerical approaches below. However, for the special case of degenerate (constant) diagonal W one finds [3] with $\eta' = 0$

$$U(t,0) = \exp(-i Wt) \exp[-i \frac{V}{\omega} \sin(\omega t)] \quad (12)$$

For two levels, the rotating wave (Rabi-[2]) solution for the population

$$p_k = P_{kk} = b_k b_k^* \quad (13)$$

of an excited level k with off-resonance shift

$$D = \omega_k - \omega_j - \omega \quad (14)$$

and the ground level j being populated at $t = 0$ ($p_j(0) = 1$, $V_{kj} \equiv V$) gives

$$p_k(t) = [V^2/(D^2 + V^2)] \{\sin[(t/2)(V^2 + D^2)^{1/2}]\}^2 \quad (15)$$

The exact solution for the special case of Eq. (12) gives

$$p_k^{ex}(t) = \{\sin[(V/\omega) \sin(\omega t)]\}^2 \quad (16)$$

corresponding to the rotating wave solution with $D^2 = \omega^2$ (since $\omega_k = \omega_j$)

$$p_k^{RWA}(t) = [V^2/(\omega^2 + V^2)] \{\sin[(t/2)(V^2 + \omega^2)^{1/2}]\}^2 \quad (17)$$

These obviously quite different expressions can be made to look more similar, if we consider the weak coupling case $V \ll \omega$ which is appropriate for the rotating wave solution as *one* condition (the other, $D \ll \omega$ cannot be satisfied in this special case), using the approximation $\sin x \simeq x$ for $|x| \ll 1$

$$p_k^{ex}(t) \simeq (V^2/\omega^2) [\sin(\omega t/2)]^2 \quad (18)$$

$$p_k^{RWA}(t) \simeq (V^2/\omega^2) [\sin(\omega t)]^2 \quad (19)$$

While this comparison of exact and rotating wave results dates back some time [3], it is of interest, that little progress has been made on further exact analytical solutions of the two level problem, which remains a challenge to the mathematician. We shall discuss the analytical solution for the infinite level case of the harmonic oscillator in section 3.

2.2 Numerical treatment of coherent excitation of many level systems with shaped, coherent infrared laser pulses

In practice, Eqs. (4–11) for the coherent excitation of many level systems have to be solved by numerical methods. For the most relevant case of quasisonant infrared multiphoton excitation one transforms to the quasisonant basis [3,4]

$$\mathbf{a} = \mathbf{S} \mathbf{b} \quad (20)$$

$$S_{kj} = \exp(in_k \omega t) \delta_{kj} \quad (21)$$

We make here use of the Kronecker Delta

$$\delta_{kj} = 1 \text{ for } k = j; \delta_{kj} = 0 \text{ for } k \neq j \quad (22)$$

and of the integer level index n_k for the quantum state k , defined by the equations

$$W_{kk} - W_{00} = n_k \omega + X_{kk} \quad (23)$$

$$-\omega/2 < X_{kk} < +\omega/2 \quad (24)$$

The easiest numerical use of this transformation is by means of the *quasisonant approximation* [3], in which we neglect all couplings corresponding to $|n_k - n_j| \neq 1$, i.e. we introduce a new coupling matrix V' which has all matrix elements corresponding to this condition equal to zero but is otherwise the same as V . This corresponds physically to neglecting fast oscillatory terms of very high frequency and leads to a differential equation with time-independent coefficients for the vector \mathbf{a} :

$$i \frac{d\mathbf{a}}{dt} = \left\{ \mathbf{X} + \frac{1}{2} \mathbf{V}' \right\} \mathbf{a} \quad (25)$$

$$V'_{kj} = V_{kj} \quad \text{for } |n_k - n_j| = 1 \quad (26a)$$

$$V'_k = 0 \quad \text{for } |n_k - n_j| \neq 1 \quad (26b)$$

The solution of Eq. (25) takes then the form

$$\mathbf{a}(t) = \mathbf{U} \mathbf{a}(0) \quad (27)$$

$$\mathbf{U} \mathbf{a}(t) = \exp\left\{-i \left(\mathbf{X} + \frac{1}{2} \mathbf{V}' \right) t\right\} \mathbf{a}(0) \quad (28)$$

This solution in the quasisonant approximation [3,4] is equivalent to the generalized rotating frame transformation solution introduced subsequently by Whaley and Light [5] and has been checked numerically on various occasions [6]. Published program packages using this approach are available since some time [7]. Extensions of this approximation are useful and have been derived for the case of strong periodic fields with highly nonresonant excitation and also for the case of fields with rather rapidly varying amplitude E_0 , which are not well described by a strictly periodic hamiltonian.

Considering first the case of a periodic field we can apply the Floquet–Liapounoff approximation [3]:

$$\mathbf{U}(t) = \mathbf{F}(t) \exp(\mathbf{A}t) \quad (29)$$

$$\mathbf{F}(0) = \mathbf{1} \quad (30)$$

$$\mathbf{F}(t + n\tau) = \mathbf{F}(t) \quad (31)$$

with period $\tau = 2\pi/\omega$ and integer $n = 0, 1, 2, \dots$, and

$$\mathbf{A}(t') = \mathbf{A}(t) \quad \text{all } t, t' \quad (32)$$

In practice one has to integrate the set of coupled differential equations for one optical cycle by any one of the common stepwise numerical integration schemes and can then derive the solution for long times by means of Eqs (29–32), which amounts to using Floquet's theory of differential equations with periodic coefficients. In a historical context we may note here, that in the Russian literature the corresponding theory is often attributed to Liapounoff [8], and we used this attribute when we introduced this method into the treatment of coherent infrared multiphoton excitation of molecules [3]. Subsequent discussions of the same method in this same context by other others [9–11] used, however, the attribute "Floquet theory" [12], as had already been done in a different, but related context by Shirley [13], prior to the discovery of infrared multiphoton excitation. In view of the obvious priority of date of Floquet's publication [8,12] "Floquet theory" may seem more appropriate. It appears, however, that quite independently, and perhaps even earlier, also Hill had derived the same mathematical theory [14]. Obviously, today's practical use [3] of the method is quite independent of its historical origin more than 100 years ago.

A second interesting extension of the URIMIR program package [7] concerns the use of excitation fields with rather rapidly varying amplitude. Indeed, the excitation dynamics with hamiltonians derived from an electromagnetic field in Eq. (1) with a slowly varying amplitude $|E_0(t)|$ can be treated in the same way as with a constant $|E_0|$. One just represents the pulse envelope as a sequence of n steps each with a constant $|E_0(t_n)|$ and uses the final condition of each step as initial condition for the next step. However, if one has strong fields with rapid variations of the field amplitude $|E_0(t)|$ on time scales not too different from the period of the field, this method is not applicable. Since the pulses are then often quite short, one may think of direct numerical integration over the whole pulse duration, still making use of the *quasisonant basis* with some advantage (but *not* using the associated *approximation*). Our calculations have shown, however, that considerable computer time can be saved by using a stepwise integration over time steps Δt using the split operator technique [15] in conjunction with the short time strong field approximation for the individual time steps, leading to the differential equation for the coefficient vector $\mathbf{b}(t)$ [3], or \mathbf{U}

matrix

$$i \frac{d\mathbf{b}}{dt} = \{\mathbf{W} + \tilde{\mathbf{V}}(t)\} \mathbf{b} \quad (33)$$

$$\tilde{\mathbf{V}}_{kj}(t) = -M_{kj} \left[\frac{2\pi}{h} \right] |E_0(t)| \cos(\omega t + \eta') \quad (34)$$

$$\mathbf{b}(t) = \mathbf{U}(t, t_0) \mathbf{b}(t_0) \quad (35)$$

$$i \frac{d\mathbf{U}}{dt} = \{\mathbf{W} + \tilde{\mathbf{V}}(t)\} \mathbf{U} \quad (36)$$

The split operator method makes use of the general approximation for the exponential function of a matrix: $\mathbf{C} = \mathbf{A} + \mathbf{B}$, where \mathbf{A} alone is already a reasonable approximation, hence [16]:

$$\exp(\mathbf{A} + \mathbf{B}) \simeq \exp(\mathbf{A}/2) \exp(\mathbf{B}) \exp(\mathbf{A}/2) \quad (37)$$

For the example of radiative excitation one finds

$$\mathbf{U}(t, t_0) \simeq \exp(-i\mathbf{W} \Delta t/2) \exp[-i\tilde{\mathbf{V}}(\langle t \rangle) \Delta t] \exp(-i\mathbf{W} \Delta t/2) \quad (38)$$

$$\exp[-i\tilde{\mathbf{V}}(\langle t \rangle) \Delta t] = \exp\left\{M_{kj} \left[\frac{2\pi}{h} \right] |E_0(\langle t \rangle)| \cos(\omega \langle t \rangle + \eta') \Delta t\right\} \quad (39)$$

The last equation shows, that the numerical effort of diagonalization for calculating the exponential function is restricted to the time independent electric dipole matrix \mathbf{M} . The matrices \mathbf{W} are diagonal (possibly complex), and hence the computation of $\exp(-\mathbf{W} \Delta t/2)$ is simple. The time step $\Delta t = t - t_0$ is much smaller than the period τ of the field, such that the coupling matrix at each time step can be approximated by its value at the average time $\langle t \rangle = (t + t_0)/2$. These equations can, of course, also be used for periodic hamiltonians in the basic integration for one field period together with Floquet theory. For further details we refer to [15]. The method is being made available also as extension of the URIMIR package for general use [17].

We may conclude here by noting that the treatment of molecular state population evolution during and after pulsed excitation includes "Raman"-like processes. When we observe population in very far off-resonance low energy states k after excitation, satisfying $E_k - E_0 \ll h\nu$ (laser photon energy) this corresponds essentially to a Raman-like process, which might be detected by measuring the population p_k instead of measuring scattered photons, as is done ordinarily in Raman spectroscopy [18]. To our knowledge no systematic investigations of the kind mentioned here, with pulsed infrared laser radiation, have been carried out. They would be much enhanced by resonance excitation in the IR. However, because of the detection of low energy state populations, which could also arise thermally, one might need to use near infrared excitation and larger energy shifts $E_k - E_0$, where resonance enhancement will be much weaker because of the inherent weakness of vibrational overtone absorption. An alternative would be to search for IR-multiphoton induced Raman like processes, where the off resonance condition would be $E_k - E_0 \ll n h\nu$ (n integer) but, of course, $E_k - E_0 \neq m h\nu$ (m integer). These types of processes deserve further study. The process described by Eqs. (16) – (19) could be characterized in the same sense as a "Rayleigh-like" process. Well known Raman like effects in the infrared, however, detected by the photon shift, are the H_2 -Raman shifted CO_2 -laser and the CO_2 -laser pumped FIR-lasers.

2.3 Quantitative transition rates under coherent and incoherent radiative excitation

In the electric dipole approximation, Eq. (3), one can express the coupling matrix element in a practical fashion as a function of radiation intensity I , in terms of angular frequency:

$$\frac{V_{kj}}{s^{-1}} = -86833957 \left[\frac{1}{D} \right] \left[\frac{I}{\text{Wcm}^{-2}} \right]^{1/2} \quad (40)$$

or perhaps even more useful in terms of wavenumbers (using more adequate intensities in the MWcm^{-2} range)

$$\frac{\tilde{\nu}_{kj}}{\text{cm}^{-1}} = -0.461 \left[\frac{M_{kj}}{D} \right] \left[\frac{I}{\text{MWcm}^{-2}} \right]^{1/2} \quad (41)$$

We have expressed here the electric dipole transition moments in the practical common unit Debye ($1\text{D} = 3.3356 \times 10^{-30} \text{Cm}$ in SI units). For intense laser irradiation the expression in Eq. (41) gives direct indication of the "power broadening" of a two level transition in terms of the common unit cm^{-1} for the wavenumber of the transition. If we look at the excitation in a two level system, Eq. (15), in terms of the time averaged excitation (or energy absorption) $\langle p_k(t) \rangle$ as a function of the wavenumber of the exciting radiation, this is a Lorentzian with full width half maximum of $2\tilde{\nu}_{kj}$ [4]. For $I = 1 \text{MWcm}^{-2}$ and $M = 1\text{D}$ one finds a width (FWHM) of 0.992cm^{-1} or just about 1cm^{-1} for an easy to remember estimate.

We may note here also the recent proposals to introduce new SI consistent units and symbols for the quantity wavenumber, similar to the unit Hertz for the quantity frequency. The proposals are to use $1 \text{Berg} = 1 \text{Bg} = 1 \text{m}^{-1}$ and to replace the difficult-to-pronounce unit cm^{-1} (or "centimeter to the power minus one") by hectoBerg = $1 \text{hBg} = 1 \text{cm}^{-1}$ [19]. The previously used unit Kayser for cm^{-1} has the disadvantage that the base unit is not the m^{-1} but the cm^{-1} , such that it would not fit into the SI system (whereas Berg and hectoBerg do). Also Kayser did not find wide acceptance. Similar to Hertz being used only for regular, not for angular frequency, Berg would be used only for regular ($1/\lambda$), not for angular wavenumber ($2\pi/\lambda$).

One can finally relate the electric transition dipole moment to the integrated absorption line strength G_{kj} between two nondegenerate, isolated quantum states k and j [20]

$$G_{kj} = \int_{\text{line}} \nu^{-1} \sigma_{kj}(\nu) d\nu = \int_{\text{line}} \tilde{\nu}^{-1} \sigma_{kj}(\tilde{\nu}) d\tilde{\nu} \quad (42)$$

$$G_{kj} = \frac{8\pi^3}{3hc(4\pi\epsilon_0)} |M_{kj}|^2 \quad (43)$$

$$\left[\frac{G_{kj}}{\text{pm}^2} \right] = 41.624 \left[\frac{M_{kj}}{D} \right]^2 \quad (44)$$

We use here the molecular absorption cross section σ in the Lambert-Beer law for absorption involving the *natural logarithm* of the ratio of incident (I_0) and transmitted intensity (I) and concentration C as a particle density over the absorption length ℓ :

$$\ell \ln(I_0/I) = \sigma \cdot C \cdot \ell \quad (45)$$

We assume absence of stimulated emission with zero concentration of the excited states for a pure absorption cross section. Eqs. (43) and (44) are valid for the *electric dipole approximation* and perfectly similar expressions can be easily written down using the *magnetic dipole approximation*, relevant for magnetic resonance and infrared transitions between levels of the same parity, for instance in the infrared absorption or laser transition $I(2P_{3/2}) - I(2P_{1/2})$ [21].

It is, however, of some interest to briefly derive the exact relations between integrated absorption line strengths and transition rates under incoherent, for instance thermal radiation, and spontaneous emission. As originally proposed by Einstein [22], the statistical transition rates between two states i and f can be written in terms of the rate coefficients of induced and spontaneous transitions

$$K_{fi}^{\text{ind}} = B_{fi} \varrho(\nu_{fi}) \quad (46)$$

$$K_{fi}^{\text{spont}} = A_{fi} \quad (47)$$

A_{fi} is the Einstein coefficient for spontaneous emission from the state i to the state f satisfying an exponential decay law

$$p_i(t) = p_i(0) \exp\left[-\left(\sum_f A_{fi}\right)t\right] \quad (48)$$

and the Einstein coefficients B for induced transitions satisfy the symmetry relation

$$B_{fi} = B_{if} \quad (49)$$

The density $\varrho(\nu)$ of incoherent radiation in terms of energy per unit volume and unit frequency (Hz) defines the units of B (mkg^{-1} in SI units). If one inserts the thermal Planck radiation density at temperature T one finds for the *total* incoherent transition rate coefficient, including both induced and spontaneous transitions [4,23]:

$$K_{fi} = A_{fi} \frac{\text{sign}(E_f - E_i)}{\exp[(E_f - E_i)/kT] - 1} \quad (50)$$

One notes the sign function $\text{sign}(x) = +1$ (-1) for $x > 0$ (< 0), which renders this transition rate coefficient nonnegative. In order to derive the relation between K_{fi}^{ind} and the integrated line strength G_{fi} in a simple fashion, we use the general relation between a first order rate coefficient and the corresponding specific bimolecular rate coefficient $k_{\text{bim.}}$ and cross section $\sigma_{fi}(\nu)$, Eq. (45), and the concentration of the collision partner [24], here photons of frequency ν [$\gamma(\nu)$]:

$$K_{fi}^{\text{ind}}(\nu) = k_{\text{bim.}}(\nu)[\gamma(\nu)] \quad (51)$$

$$k_{\text{bim.}}(\nu) = c \cdot \sigma_{fi}(\nu) \quad (52)$$

We note that the relative velocity of photons and molecules is just c . The total rate coefficient K_{fi} for transitions in a statistical (e.g. thermal) radiation field of energy density $\varrho(\nu)$ is obtained by integration over all contributing frequencies of the line

$$K_{fi}^{\text{ind}} = \int_{\text{line}} \sigma_{fi}(\nu) c [\gamma(\nu)] d\nu \quad (53)$$

The concentration of photons of frequency ν is simply related to the corresponding energy density, hence

$$[\gamma(\nu)] = \varrho(\nu)/(h\nu) \quad (54)$$

$$K_{fi}^{\text{ind}} = \frac{c}{h} \int_{\text{line}} \sigma_{fi}(\nu) \varrho(\nu) \nu^{-1} d\nu \quad (55)$$

For a constant energy density $\varrho(\nu)$ or by taking $\varrho(\nu)$ equal to the approximately weighted average over the line profile, we can take it as $\varrho(\nu_0)$ in front of the integral, resulting in the desired relation

$$K_{fi} = \frac{c}{h} \varrho(\nu_0) G_{fi} \quad (56)$$

In practice, we may set $\nu_0 = \nu_{fi}$ at the center frequency of the line. One thus has the relation to the various Einstein coefficients [20]

$$G_{ul} = \frac{h}{c} B_{ul} = \frac{c^2}{8\pi\nu_{ul}^3} A_{lu} \quad (57)$$

We have used here the indices for upper (u) and lower (l) states to show the necessary asymmetry in the rate coefficient for spontaneous emission A_{lu} . In deriving these relations, no use is made of electric dipole, magnetic dipole or any other such approximation. Thus Eq. (57) is valid for all incoherent statistical one-photon transitions, irrespective of their dynamical origin. The relation to the electric dipole approximation can be made by Eq. (43) or related equations for other types of transition. The equations are valid for nondegenerate quantum states i and f . For degenerate levels appropriate sums over final states and averages over initially populated states have to be carried out. If induced emission is negligible, one has for a transition between levels n and m with degeneracy g_n and g_m and populations $p_{i(m)}$ in the lower level only:

$$G_{nm} = \sum_{i=1}^{g_m} \sum_{f=1}^{g_n} p_{i(m)} G_{fi} \quad (58)$$

If the upper levels have some thermal (or other) population, induced emission is important and one may wish to define a net integrated absorption intensity

$$G_{nm}^{\text{net}} = \sum_{i=1}^{g_m} \sum_{f=1}^{g_n} (p_{i(m)} - p_{f(n)}) G_{fi} \quad (59)$$

From the equations given, the relevant integrated line strengths (or band strengths) emerge naturally by *logarithmic* integration of absorption cross sections $\sigma(\nu)$ over $d\ln\nu$ or $\nu^{-1}d\nu$ (or similarly $d\ln\tilde{\nu}$ or $d\ln\omega$ etc.). Another line strength S is also commonly used

$$S = \int_{\text{line}} \sigma(\tilde{\nu}) d\tilde{\nu} \approx \frac{1}{\tilde{\nu}_0} G \quad (60)$$

Whereas G has the dimension of a cross section, i.e. a surface, S has the dimension of a length and the last equality in Eq. (58) is only approximate with $\tilde{\nu}_0$ being the center wavenumber of the line (or band). We have repeatedly stressed the usefulness of G as a measure for line strength or band strengths of chromophores and it seems that R. Mecke, to whom this journal issue and conference are dedicated was among the first (perhaps even the first), to stress the importance of logarithmic integration for band strengths [20]. Since quantities other than G are frequently used we discuss some of the relations and give also some quantitative results for certain infrared chromophores, which are of particular interest for radiative transitions.

2.4 Integrated band strengths of infrared chromophores

For rather unfortunate reasons in the historical development of quantitative infrared spectroscopy, the important quantity integrated line strength or band strength (integrated over a vibrational band in the latter case, using Eq. (42) or similar ones) is frequently both poorly measured and reported in a variety of sometimes ill defined units. We summarize in table 1 the most important ones [25].

Table 1
Quantities commonly used in reporting integrated line- or band strengths (see [25]) with practical conversion to G

Quantity	Common unit	Conversion to G
\bar{A}	km mol^{-1}	$(G/\text{pm}^2) = 16.60540 \frac{(\text{A}/\text{km mol}^{-1})}{\tilde{\nu}_0/\text{cm}^{-1}}$
\bar{S}	$\text{atm}^{-1} \text{cm}^{-1}$	$(G/\text{pm}^2) = 0.01362603 \frac{(\text{S}/\text{atm}^{-1} \text{cm}^{-1})(\text{T}/\text{K})}{(\tilde{\nu}_0/\text{cm}^{-1})}$
S	cm	$(G/\text{pm}^2) = 10^{20} \frac{S/\text{cm}}{(\tilde{\nu}_0/\text{cm}^{-1})}$
Γ	$\text{cm}^2 \text{mol}^{-1}$	$(G/\text{pm}^2) = 1.660540 \times 10^{-4} (\Gamma/\text{cm}^2 \text{mol}^{-1})$
G	pm^2	$(G/\text{pm}^2) = (G/\text{pm}^2) = 10^{24} (G/\text{m}^2)$

The general equations connecting the various quantities are (in part approximately)

$$G = \Gamma/N_A = \bar{A}/(\tilde{\nu}_0 N_A) = S/\tilde{\nu}_0 = \bar{S}(kT/\tilde{\nu}_0) \quad (61)$$

We have used here \bar{A} instead of the commonly used A for the band strength associated with the commonly used " km mol^{-1} " in order to avoid confusion with both the symbols A for the Einstein coefficient for spontaneous emission and A_e for absorbance. Note that G has the same dimension and unit as the molecular absorption cross section σ . We have in the past investigated systematically the band strengths of strong infrared chromophores, particularly suitable for excitation with infrared lasers. In the CO_2 laser range around 1000 cm^{-1} (hBg) we may mention the isolated CF chromophore in mono-fluorinated saturated hydrocarbons, with $G(\text{CF}) \approx 1.7 \text{ pm}^2$ [26]. This is rather independent upon the chemical environment and among the strongest chromophores, together with the SO chromophore in sulfoxides, with $G(\text{SO}) \approx 2.0 \text{ pm}^2$ somewhat dependent upon the chemical environment. In contrast the much weaker alkyl-CH

chromophore in organic compounds shows very strong variations upon the local chemical environment, with values of G for the fundamental transition near 3000 cm^{-1} ranging from 0.002 pm^2 in CHCl_3 to 0.13 pm^2 in CHF_3 , a variation, which can be well described by a simple group contribution rule equation [27]. The CH chromophore is also quite interesting for overtone transitions [28]. There is roughly a decrease in G by about one order of magnitude for each additional quantum of excitation of CH stretching. This decrease is more pronounced for the molecules with the strongest fundamental transition, less pronounced for molecules with the weakest fundamental, such that for the $N = 4$ CH stretching overtone one has convergence for all compounds with $G \approx (4 \pm 2) \text{ fm}^2$ for each alkyl CH [28, 29]. This behaviour can be rather well modelled by the one-dimensional bond dipole model pioneered by Mecke and coworkers [28, 30-32], although further analysis shows in fact the necessity of more complex dipole moment hypersurfaces at least in the three strongly coupled degrees of freedom of the CH chromophore [33-35]. We note the easy accessibility of the $N = 4$ alkyl-CH overtone near 11400 cm^{-1} to the strong NIR-radiation from the Ti-Sapphire laser [36]. We shall now address the question of the dynamical response of infrared chromophores to coherent infrared radiation for the simple model problem of a well separable harmonic oscillator normal vibration and for anharmonic, coupled vibrations in real polyatomic molecules.

3. THE HARMONIC OSCILLATOR COHERENT AND IRREGULAR MOTION

The stationary states of the quantum harmonic oscillator and their graphical display are standard textbook examples for illustrating vibrational motion and the classical harmonic oscillator motion is part of the pre-university physics school teaching in most civilized countries. However, the coherent quantum oscillation of the harmonic oscillator is not widely taught, although it was among the first examples used in time dependent quantum mechanics [37]. We shall provide here a somewhat didactic demonstration of the dynamics of the quantum harmonic oscillator under coherent and incoherent excitation, noting, however, that even in recent times a few new results have been obtained on this simple system. The harmonic oscillator may serve as a simple model for the description of vibrational motion in a diatomic molecule. The harmonic oscillator is also the starting point for the simplest description of the dynamics of polyatomic molecules in terms of harmonic normal vibrations [38].

3.1 Coherent radiative excitation of the harmonic oscillator

As other N -level systems, the harmonic oscillator of frequency Ω in a coherent radiation field of frequency ω can be treated numerically to within the approximations defined in section 2.2. However, a particular feature of the harmonic oscillator is the possibility of an exact closed expression solution of the time dependent quantum equations of motion, Eqs. (4-11). It seems that the first such solution was given by Ludwig in 1951 [39], with subsequent, apparently independent work by others [40-45]. While the problem thus seems to have been well treated over the years, we have noted recently that the harmonic oscillator excitation can also be solved exactly in the generalized rotating wave or quasisresonant approximation (QRA, [46]). It provides thus a unique possibility to illustrate the validity and breakdown of this approximation. The results of [46] can be summarized by the equations for the probability density $|\Psi(q,t)|^2$ and level populations $p_n(t)$, where we note a change of definitions (ω and Ω) to be consistent with our notation in section 2.

$$|\Psi(q,t)|^2 = \pi^{-1/2} \exp\{-[q - q_0(t)]^2\} \quad (62)$$

$$\Psi(q, t = 0) = \pi^{-1/4} \exp(0.5 q^2) \quad (63)$$

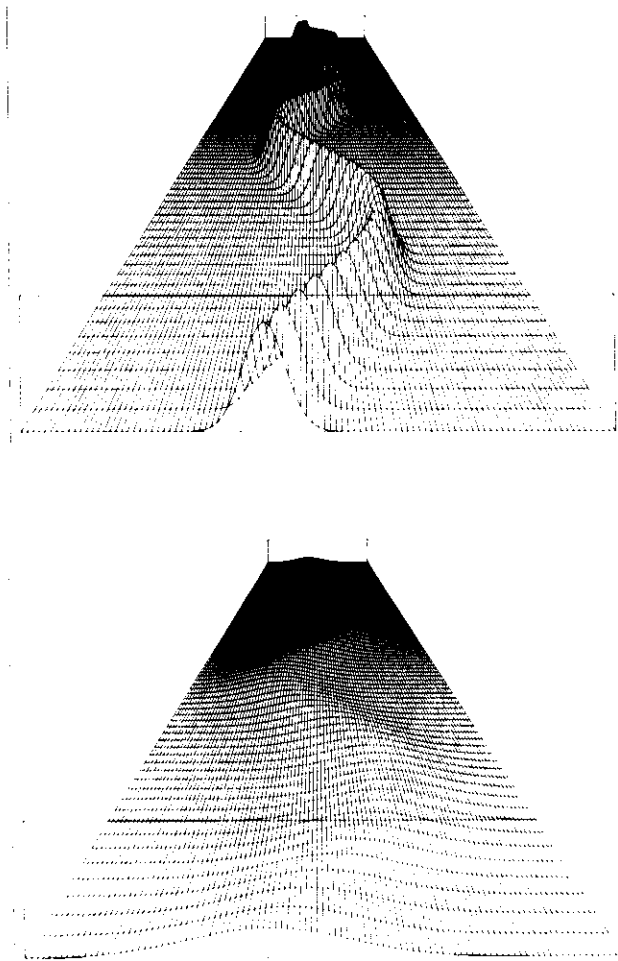


Figure 1: Probability density of the harmonic oscillator under coherent excitation. In the example we have chosen $\tilde{\nu}_{\text{Oscillator}} = 1000 \text{ cm}^{-1}$, $\tilde{\nu}_{\text{Laser}} = 999 \text{ cm}^{-1}$, $M_{10} = 0.5D$, linear dipole, i.e. $M_{v+1,v} = M_{10} (v+1)^{1/2}$, $I = 100 \text{ MW cm}^{-2}$, time from 16.5 to 16.6 ps. The time step (backwards in the perspective figure) is 1 fs. Coordinate axis q from left to right, probability density on vertical axis. (a) Coherent excitation with the oscillator initially in the ground state. (b) Coherent excitation of an ensemble with density matrix corresponding initially to 10000 K, which corresponds to a broadened Gaussian probability density, as is well known (by permission from [47,48]).

$$q_0(t) = -V_{01} \Omega 2^{-1/2} (\Sigma\Delta)^{-1} \sin(\Sigma t) \sin(\Delta t) \quad (64)$$

$$\Sigma = 0.5 (\omega + \Omega) \quad (65)$$

$$\Delta = 0.5 (\Omega - \omega) \quad (66)$$

$$p_n(t) = (n!)^{-1} [M(t)]^n \exp[-M(t)] \quad (67)$$

$$M(t) = 0.25 V_{01}^2 [\Delta^{-2} \sin^2(\Delta t) + \Sigma^{-2} \sin^2(\Sigma t) + 2 \cos(\omega t) (\Sigma\Delta)^{-1} \sin(\Sigma t) \sin(\Delta t)] \quad (68)$$

The p_n follow a Poisson distribution with maximum at $M(t)$. $q_0(t)$ describes the classical trajectory of the forced oscillator in configuration space and the time dependent probability density in q -coordinate space is just a Gaussian centered at this value. Perfectly similar results arise for the density in p -momentum space. V_{01} is the coupling between levels 0 and 1 as defined by Eq. (3). In the quasiresonant approximation one finds similar equations, replacing q_0 by

$$q_0^{\text{QRA}}(t) = -V_{01} 2^{-1/2} \Delta^{-1} \sin(\Sigma t) \sin(\Delta t) \quad (69)$$

and $M(t)$ by

$$M_{\text{QRA}}(t) = \frac{V_{01}^2}{4\Delta^2} \sin^2(\Delta t) \quad (70)$$

One thus finds relative errors for the quasiresonant approximation

$$\left| \frac{q_0(t) - q_0^{\text{QRA}}(t)}{q_0(t)} \right| = \left| \frac{\Delta}{\Omega} \right| \quad (71)$$

$$\left| \frac{M(t) - M_{\text{QRA}}(t)}{M_{\text{QRA}}(t)} \right| = \left| \frac{\Delta^2 \sin^2(\Sigma t) + 2 \cos(\omega t) \frac{\Delta \sin(\Sigma t)}{\Sigma \sin(\Delta t)}}{\Sigma^2 \sin^2(\Delta t)} \right| \approx \left| \frac{\Delta}{\Sigma} \right| \quad (72)$$

These errors are obviously small, if the resonance defect $|\omega - \Omega| = |2\Delta|$ is small compared to the fundamental frequency Ω . The error does not seem to depend upon the strength of the coupling V_{01} , proportional to the square root of the radiation intensity. However, as discussed in [46], in practical numerical applications of the quasiresonant approximation, one would truncate the infinite level system to some finite number, and the truncation error does, indeed, depend on V_{01} . We have given here only the simplified expressions with the phase of the field $\eta = 0$. For the general expressions and derivations we refer to [46]. We conclude here by providing graphical representations of the probability density of the harmonic oscillator under coherent excitation, both from the solution of the Schrödinger equation for a pure state [47] and from the solution of the Liouville von Neumann equation for an ensemble with a density matrix at $T = 10000 \text{ K}$ initially [48] in Figs. 1a and 1b.

3.2 Incoherent radiative excitation of the harmonic oscillator

The incoherent excitation of the harmonic oscillator by a thermal black body radiation field seems to have found attention only recently [49]. In the statistical limit of the master equation for an ensemble in a black body Planck-radiation field [4], one has for the populations p_n of levels in matrix notation

$$\frac{d\mathbf{p}}{dt} = \mathbf{K} \mathbf{p} \quad (73)$$

$$\mathbf{p}(t) = \exp(\mathbf{K}t) \mathbf{p}(0) \quad (74)$$

The matrix elements K_{fi} are given by Eq. (50) and for a linear dipole function they are nonzero only for adjacent levels of the harmonic oscillator by means of Eqs. (44) and (57). The time dependent populations $p_n(t)$ are quite different from the Poisson distribution of coherent excitation. Depending upon initial condition and radiation temperature, they may show smooth, monotonous relaxation towards thermal equilibrium or go through maxima [49]. When one compares typical excitation times from the ground state, a typical CO_2 laser excitation with 100 MW cm^{-2} of a harmonic oscillator with $\tilde{\nu} \approx 1000 \text{ cm}^{-1}$ would correspond to "equivalent kinetic temperatures" of the radiation field of about 10^{12} K , in order to obtain similar thermal excitation rates. This provides some instructive orders of magnitude. The long time limit in thermal excitation is, of course, the Boltzmann distribution $p_n \propto \exp(-n\hbar\nu/kT)$, which is an almost linearly decreasing function of n for small n and high temperatures with $\epsilon = \hbar\nu/kT \ll 1$, hence $p_n \approx \epsilon(1-n\epsilon)$, which may be compared to the quite different behaviour from Eq. (67).

The kinetic Eq. (74) for the ensemble average provides us only with populations p_n , not with time dependent wavefunctions or coefficients $b_n(t)$ in the expansion of Eq. (8). One may nevertheless simulate a typical individual member from the ensemble by randomly drawing from such an ensemble a state vector of the harmonic oscillator consistent with the constraint placed by the $p_n(t)$, for example by selecting

$$b_n(t) = \sqrt{p_n(t)} \exp(-i \alpha_n t) \quad (75)$$

$$\alpha_n(t) = \alpha_n(t_0) + n\Omega(t - t_0) \quad (76)$$

$$0 < \alpha_n(t_0) < 2\pi \quad \text{random} \quad (77)$$

The random selection (practically from a random number generator) of the $\alpha_n(t_0)$ introduces an element of irregularity into the dynamics of the harmonic oscillator. This irregularity can be made even more pronounced, if we assume a random phase $\alpha_n(t)$, by strong random interaction with the radiation field at all times. This behaviour is

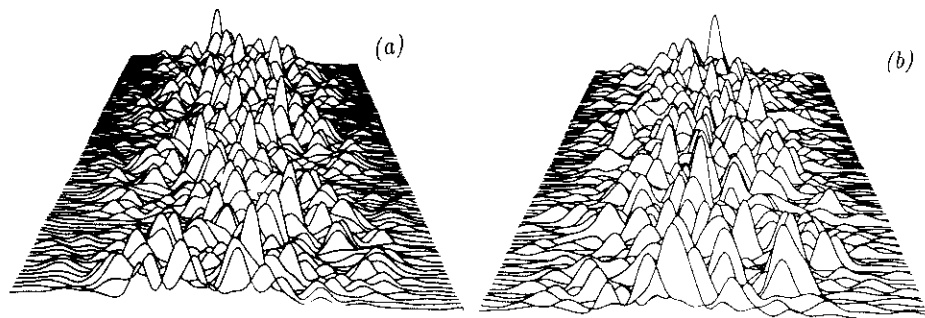


Figure 2: Probability density of the harmonic oscillator under thermal excitation with 10000 K radiation temperature and parameters otherwise as in Figure 1. The time step is again 1 fs , but the times shown start 4 ns after thermal excitation from the ground state. (a) shows the behaviour using Eqs. (75) – (77). (b) has random phases at all times (see text, by permission from [49]).

illustrated in Fig. 2 by typical probability densities for the single harmonic oscillator drawn from thermally excited ensembles by these prescriptions [49].

Fig. 2 may be nicely compared to Fig. 1. We stress that we show the dynamics of one *typical member of the ensemble*. The probability density $P(q)$ for a thermal ensemble of harmonic oscillators is simply a broad Gaussian, as is well known [48]. These results for the harmonic oscillator provide instructive insight for the simplest model of the dynamics of polyatomic molecules under infrared excitation, i.e. the treatment in the harmonic normal mode limit. In that limit, the dynamics would just be the superposition of the dynamics of a collection of uncoupled harmonic oscillators [38]. For coherent excitation, the quantum dynamics would be, indeed, quasi-classical. In reality, however, anharmonic coupling leads to quite a different behaviour, which we shall address now.

4. MOTION IN POLYATOMIC MOLECULES: COUPLED ANHARMONIC VIBRATIONS

We have in our previous review [1] already quite extensively discussed the various time scales for intramolecular rovibrational couplings in real polyatomic molecules. It turns out that the ideal picture of quasiclassical harmonic normal mode vibrational motion in polyatomic molecules is very far, indeed, from reality. In actual fact, the motion is highly anharmonic, nonclassical and very diverse, as far as different types of vibrational modes in chemical structures are concerned. For various aspects of this question we refer to the reviews in [1,20,50]. Here we shall mainly address two more recent observations. The first one concerns the nature of the time dependent probability density in one vibrational coordinate of a mode, which is strongly coupled to others [15,51]. This can be related to our discussion of the harmonic oscillator in section 3. The second one concerns the systematic investigation of symmetry breaking on vibrational mode-coupling in the CH chromophore in organic molecules exhibiting various symmetries [50–53].

4.1 Time dependent probability density in one vibrational mode strongly coupled to others

Our investigations over the last decade have shown that for the alkyl–CH chromophore one finds rather generally anharmonic vibrational redistribution between the CH stretching and the CH bending modes on a time scale of about 100 fs , leading essentially to a quasimicrocanonical equilibrium of these three modes in about this time. Other vibrational modes participate only on much longer times, i.e. there is a pronounced separation of time scales [54,55]. While this behaviour depends still upon the symmetry of the molecule involved, as we shall discuss below, it is otherwise rather similar for all organic molecules, which have been investigated, so far, with numerous substitutions. The behaviour is well reflected by the complexity of the overtone spectra in the infrared and visible ranges.

In order to illustrate the vibrational motion corresponding to this redistribution process in some more detail, we may consider the time dependent probability density under coherent infrared excitation both for the initially excited CH stretching mode and for the CH bending modes accepting the energy from the excited mode. In order to obtain a one-dimensional representation of the multidimensional problem, we represent the one dimensional probability density $P(q_s, t)$, say, in the CH stretching coordinate q_s , integrating over the other modes:

$$P(q_s, t) = \iint |\Psi(q_s, q_i, q_0)|^2 dq_i dq_0 \quad (78)$$

In a molecule with a C_s symmetry plane, such as CHD_2F , q_i would be the CH–bending

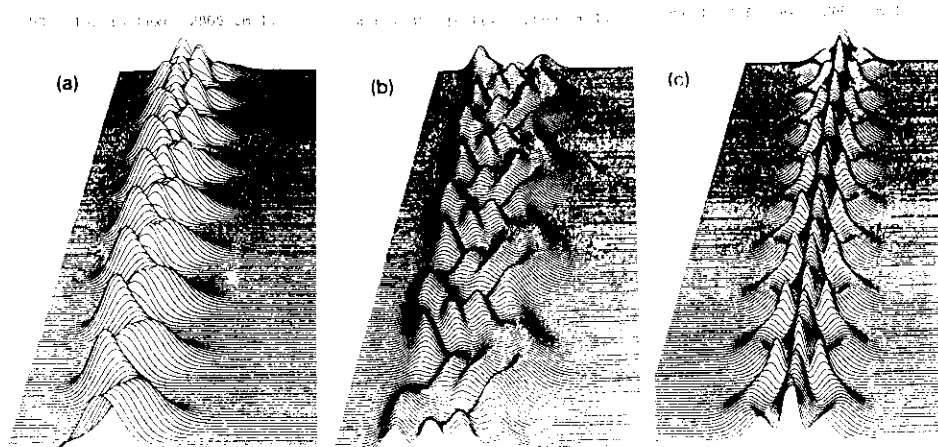


Figure 3: Time dependent probability densities from Eq. (78) calculated with a spectroscopic hamiltonian under coherent excitation of CH stretching in CHD_2F at a radiation wavenumber of 2865 cm^{-1} and 20 TW cm^{-2} . (a) The abscissa shows the range of dimensionless normal coordinate $-4.5 < q_s < +8.5$, time step separating two lines towards the back is 0.5 fs in the time range 50 to 150 fs after start of radiative excitation. (b) as (a) but from 400 to 350 fs with time step 0.25 fs . (c) as (a) but showing $P(q_i, t)$, integrated over q_s and q_o , otherwise as in Eq. (78), time range 950 to 1050 fs , time step 0.5 fs , coordinate range $-8 < q_i < +8$. (by permission from [51]).

coordinate in the C_s symmetry plane and q_o is CH bending perpendicular to this plane. Of course, one can define perfectly similar probability densities $P(q_i, t)$ and $P(q_o, t)$ by integrating over the corresponding other coordinates.

Fig. 3 shows such a probability density obtained for CHD_2F under coherent excitation near the CH stretching fundamental frequency, using a hamiltonian derived from spectroscopic analysis [51]. Fig. 3a may well be compared with the coherent harmonic oscillator motion in Fig. 1. Initially, for about 10 vibrational periods, there is similar quasiclassical motion. However, due to anharmonicity, the wavepacket breaks up in a nonclassical way at longer times (Fig. 3b) and shows even more complex behaviour at longer times. Fig. 3c shows how excitation arrives in the bending mode at times around 1 ps, when the CH stretching mode is coherently excited. Substantial bending excitation is found at this time, also for the out of plane mode, which is not shown.

The nonclassical quantum breakup in the density (Fig. 3b, c) has also been demonstrated in two dimensional representations for CHF_3 [34]. One may wonder, whether there is also similar behaviour to the incoherently driven harmonic oscillator analogous to Fig. 2 to be found in polyatomic molecule dynamics. Indeed, it has been surmised – but so far not proven by complete experimental analysis – that the weaker coupling to the numerous vibrational modes in a large polyatomic molecule can be described by a Pauli master equation of a form similar to Eq. (73), which would lead to precisely such a quantum statistical behaviour of the probability density [56]. The difficulty in the experimental analysis of this phenomenon resides in the very high complexity of the resulting spectra, which is very demanding in the hamiltonian analysis of modest and weak couplings of skeletal modes in polyatomic molecules, as we have repeatedly, and recently again shown for CF_3I [57–59]. While only a full hamiltonian analysis will allow for complete understanding of the quantum statistics,

one may obtain a preliminary analysis in terms of statistical models for line distributions and intensities of "global vibrational states" [60]. One can also systematize the analysis in terms of fundamental symmetries, which we shall briefly discuss now.

4.2 Symmetry breaking couplings in C_{3v} , C_s and chiral C_1 molecules

Fig. 4 shows the coordinates of a CH chromophore in the environment of a CX_3 skeleton of various symmetries. In simple terms, the short time dynamics of the CH chromophore on a heavy skeleton is governed by three coupled normal vibrations which are closely related to the three polar coordinates r , ϑ and φ shown in the Figure.

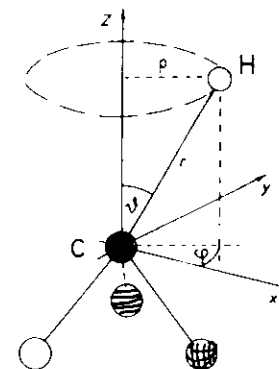


Figure 4: Coordinates of the CH chromophore on a heavy skeleton with various symmetries (C_{3v} , C_s , C_1).

One can discuss the dynamics in terms of a systematic symmetry reduction and corresponding symmetry breaking. The highest effective symmetry, found for the strong Fermi resonance in C_{3v} – CX_3H molecules corresponds to a hamiltonian with $C_{\infty h}$ symmetry. For this symmetry the quantum number l corresponding to vibrational angular momentum about the C_{3v} symmetry axis (z) of the CX_3 skeleton (rotation in φ) is a good quantum number, approximately conserved in the course of motion at least for short times. The analysis of the spectra of CX_3H compounds is, indeed, consistent with this high symmetry, the hamiltonian being block diagonal in l . The weak couplings between the blocks lead to little consequences in the spectra, which have not been fully analyzed in these terms. However, when using *ab initio* potentials, which show, of course, only the reduced C_{3v} symmetry (not $C_{\infty h}$), the l -violating populations could be shown to remain under the 5% level even with purposeful overestimate of the couplings [52]. The dynamical problem corresponds effectively to two coupled vibrations in (r, ϑ) space.

However, when reducing the symmetry to C_s by substitution (including isotope substitution) one finds essentially complete removal of the l -conservation, the effective dynamical symmetry being, indeed, equivalent to the C_s point group. The dynamics correspond to three strongly coupled vibrations on short time scales, the A' , A'' symmetries remaining, however, good quantum numbers in the dynamics, as expected. The example of CHD_2F , which we have discussed in section 4.1 belongs to this class [15,51] and there are further examples, such as $\text{CFHC}\ell_2$, $\text{CF}_2\text{HC}\ell$ and $(\text{CF}_3)_2\text{CFH}$ [61,62]. The next step in this analysis is to reduce the symmetry to C_1 . We could establish recently that in chiral molecules, which have C_1 symmetry either by isotopic substitution, such as CHDTF , or by elemental substitution, such as $\text{CHF}\ell\text{C}\ell\text{Br}$, the A' , A'' dynamical symmetry is effectively violated on the 100 femtosecond to 1 ps time

scale, the effective coupling matrix elements between vibrational A' and A'' symmetry being derived from the fundamental coupling constant $k_{\text{gab}}^* \approx 20 \text{ cm}^{-1}$ in these systems [53]. We shall not pursue here further details of this problem but rather return now to the question of more fundamental dynamical symmetries in C_1 chiral molecules, which we had briefly addressed two years ago [1], and which in the meantime has obtained further attention.

5. SYMMETRY VIOLATION AND CONSERVATION LAWS IN INTRAMOLECULAR DYNAMICS: TESTS OF C, P, T VIOLATION IN CHIRAL MOLECULES

Motto

Nissuna humana investigatione si puo dimandare vera scientia, se essa non passa per le matematiche dimostrazioni e se tu dirai, che le scientie que principiano e finiscono nella mente habbiano verita, questo non si concede, ma sie nega, per molte ragioni e prima, che in tali discorsi mentali non accade esperienza, senza la quale nulla da di se certezza.

(No human inquiry can claim the status of true knowledge without passing through mathematical demonstration: and if you say that sciences which begin and end in the mind possess truth, this cannot be allowed, but must be denied for many reasons: and first of all because experience does not enter into such mental exercises, and without it, there is no certainty.)

Leonardo da Vinci (as cited and translated in "The Vision of Nature" by Cyril N. Hinshelwood)

Chiral molecules have interesting "hidden" symmetries in their dynamics, even with their apparently asymmetrical C_1 structures. Thus the dynamical symmetry reduction discussed in section 4 actually does not stop, when we arrive, say, at a chiral C_1 molecule such as $\text{CHFC}\ell\text{Br}$ [50]. There remains the quantum number *parity* which should be a good quantum number in the course of the short time dynamics. On longer times this symmetry may be violated, in fact, we expect this to happen, although this has not yet been proven experimentally. More precisely, we can form superposition states of left handed (L) and right handed forms (R) of the chiral C_1 molecules. These superpositions may have a well defined symmetry or parity (+ or -) with respect to the space inversion of all coordinates. However, with parity violation, this quantum number may change in the course of time [63,64]. The time for parity transfer is directly linked to a parity violating energy difference ΔE_{pv} by Eq. (79) [1]:

$$t(+ \rightarrow -) = \frac{1}{2} \tau_{\pm} = \frac{1}{2} \left[\frac{\hbar}{2\Delta E_{\text{pv}}} \right] \quad (79)$$

ΔE_{pv} is the hypothetical energy difference between the ground states of the left handed (L) and the right handed molecule (R). If $\Delta E_{\text{pv}} = 0$, parity will be strictly conserved in the dynamics of the chiral molecule. Current theoretical estimates would suggest, however, interconversion times $t(+ \rightarrow -)$ of the order of hours or days, i.e. rather long but not infinite (and perhaps measurable [63,64]).

In [1] we have further complemented the two isomers L and R by adding to this a scheme with two further "isomers" corresponding to the left handed (L^*) and right handed molecules made of antimatter (R^*). Very similar to the question of parity violation, further energy differences such as ΔE_{cpv} between L and R^* (or L^* and R) correspond to further symmetry violation (C stands for charge conjugation [1]). Indeed, if one could measure an energy difference ΔE_{cpv} this could be used to test some of the

most fundamental symmetries of nature. It was suggested in [1] to devise some experiments to test for such energy differences implying CP and CPT violation, and we have in a lecture for a community of physicists [65] proposed still somewhat hypothetical experiments on antimatter chiral molecules, which would test for CP and CPT violation in molecular physics and therefore would be a fundamental molecular test of the equivalence of particles and antiparticles, at a level of precision far beyond current high energy physics results of the proton and antiproton mass equivalence [66]. One of the proposed experiments is a direct extension of our earlier proposal for measuring parity violation by means of a time dependent molecular "motion" [63]. Subsequently the question of CPT violation in relation to the hypothetical ΔE_{cpv} was discussed in considerable mathematical detail [67] and it was concluded that CPT symmetry violation might be unlikely, thus excluding a measurable ΔE_{cpv} . We think, however, that the questions of the fundamental symmetry violations of charge conjugation C, parity (P) and time reversal (T) and of combinations such as CP and CPT symmetries in molecular physics remain among the *open questions*.

The conclusion as in [1] is, that experiment and only experiment can provide the answer as to possible CP-violating energy differences ΔE_{cpv} in enantiomeric matter-antimatter molecular pairs (Fig. 7 of [1]). This is in agreement with the general point of view expressed earlier by the authors of the *Motto* cited above. While one might stop here, it may be useful to add some remarks, why one might hope for a nonzero result in the first place, and why such a result would be interesting in the second place. The following intuitive remarks are necessarily purely speculative.

(i) The history of the symmetry violations C,P,T (and CP, CPT etc.) including finally also the generalized Pauli principle somehow suggests that perhaps in the end one will find de lege violations of all the discrete symmetries [1].

(ii) As we have discussed elsewhere [1,68], without CP violation we would not be able to establish, in an absolute sense, the structure of aminoacids, because L and R^* (or R and L^*) pairs would be equivalent. In a different (and more general) context such questions have also been discussed by Lee [69]: The absolute structure (i.e. L or R^*) would be "non-observable" (including the matter antimatter ambiguity). However, in actual fact we *can* establish the absolute structure (of L or R^*) indirectly by using CP violation in the K^0 meson decay [1]. One might think therefore, that perhaps the absolute structure (R^* , L, L^* , R) might also already be revealed directly, for instance by slight differences in the ground state energies and structural properties. In the absence of a quantitative theory of the connection between these phenomena one *cannot*, however, predict if and how this is going to happen, and therefore an experiment (direct or indirect with added theoretical knowledge) is necessary, as we have been careful to point out before [1] (after all, K^0 meson decay is currently believed to be CPT symmetric to within about 10% uncertainty compared to the established CP violation [70]). Complex time dependent kinetic phenomena would also be of interest, here. As we have discussed [71], the kinetics of the biochemistry of living species of our "L-aminoacid world" might be fundamentally different from the "D-aminoacid world" (which could be tested experimentally and, by extension also from L^* and D^* -aminoacid worlds (difficult to test, indeed).

(iii) Our last point refers to the importance of investigating the small (hypothetical) energy differences in the scheme of Fig. 7 of ref. [1]: Why should anyone be interested in the outcome of such experiments anyway? In our world including living species we do observe (in terms of the aminoacid components of proteins) only "L" of the four possibilities. The other three possibilities (L^* , R^* , R) have been removed by first selecting matter over antimatter in the big bang and then L over R in evolution [1,68]. Now, this selection might be "de facto" or "de lege", the former referring to a situation, where *some* selection is necessary, but it doesn't matter what one selects, the latter to a situation, where there is a preferred selection of one specific form (here "L") over the others. At present we do not know enough to decide between the "de facto" and the "de lege" explanations. In principle an " R^* " world might be

equally possible. It is often argued, that the energy differences (if any!) of the isomers L, R, L*, R* are certainly so small, that the selection will be de facto anyway, and therefore establishing some small bias is irrelevant for the questions posed [72]. We shall illustrate the limitations of this reasoning by the analogy with a game, which we may call with some modest justification "the world game". It consists of a game leader drawing arbitrarily tetrahedral dice from two boxes, (a) the "de facto" box, where each dice has four different faces (denoted L, R, L*, R*) and the "de lege" box (four types of dice, each one having only one letter on all four faces, say L, or else R, L*, R*). The players are allowed to make just *one* throw with the selected tetrahedral dice and observe the *one* face of the tetrahedron showing towards them. Then the players, who may be called also the "scientists", must guess, from which box the dice has been drawn, i.e. what are the "rules of the game" (de facto or de lege, there will be a reward for the right guess of the rules of the game, as there might be in science). Now, if the "de lege" box has equal numbers of each dice ("L", "R", "L*" and "R*") and if the game leader is a statistically honest person, the statistics is fairly simple and the player does not have much of a winning strategy against other players. If one player knows, however, that the de lege box contains a bias towards one type of dice (say 40% L and 20% each of the others), he will win with the strategy of guessing "de lege" if he sees an "L" in the single throw and "de facto" if he sees any of the other faces. In fact, however small the known bias is, in the long run he will *always* win over those who don't know the bias and that is, why it is important to know the bias, also in the analogous physical situation. One obvious conclusion concerning the physical situation in biochemical evolution can be drawn from the single observation of an L-aminoacid world: The bias *cannot* be 100% in favour of any combination of R*, R, L*.

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