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Molecular Spectra, Reaction Dynamics, Symmetries and Life[#]

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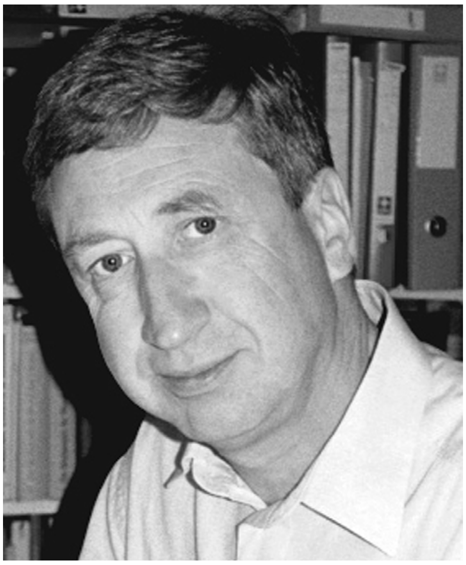
Paracelsus Prize Winner 2002

Dedicated to Jack D. Dunitz on the occasion of his 80th birthday

Abstract: We provide a short review of the work of the group for molecular kinetics and spectroscopy at the Laboratory for Physical Chemistry of ETH Zürich contributing to our understanding of the fundamental physical-chemical primary processes in chemical reactions. After a brief historical introduction, we present a selection of recent progress and thinking in three areas:
1. Experiments in high resolution molecular spectroscopy leading us from an elucidation and unraveling of molecular infrared spectra to the understanding of the molecular reaction dynamics and fast intramolecular processes from the nanosecond (1 ns = 10^{-9} s) to the femtosecond (1 fs = 10^{-15} s) and even sub-fs or attosecond (1 as = 10^{-18} s) domain.
2. Theory of fundamental symmetries of physics and their violations in molecular spectra and dynamics of chiral molecules with a discussion of possible consequences for the role of chirality in the origin of life.
3. Speculative considerations on the relationship of spectra and dynamics of chiral molecules with the CPT theorem of physics and with the origin of matter and chiral life, and on the relationship of time reversal symmetry violation with the molecular origin of irreversibility and with the possible molecular origin of thought.

Keywords: Chirality · CPT theorem · Fundamental symmetries · High-resolution infrared spectroscopy · Molecular reaction kinetics · Origin of life · Parity violation · Quantum dynamics



Martin Quack studied in Darmstadt, Grenoble and Göttingen, where he received his chemistry diploma in 1971 working on his diploma thesis on high-resolution fluorescence spectroscopy with Manfred Stockburger and Albert Weller at the Max-Planck-Institutes for Spectroscopy and Biophysical Chemistry. He received his doctoral degree from the Ecole Polytechnique Fédérale de Lausanne in 1975 after work with Jürgen Troe in reaction kinetics. As Max Kade Fellow he stayed with William H. Miller at the University of California Berkeley 1976/77 and habilitated in Göttingen in 1978, where he was Privatdozent and later Professor (C2) until 1982. In this year he was appointed full professor at the University of Bonn and in 1983 was elected Professor Ordinarius for Physical Chemistry at ETH Zürich, where he has been since then. Chemistry with its sometimes striking transformations through the processes of molecular kinetics, spectroscopy and fundamental symmetries in nature leading to conservation laws and their subtle violations have been his scientific hobbies ever since his school days. He has been honored for his work in these areas for instance by the Nernst-Haber-Bodenstein Prize, the Otto Klung Prize and the Otto Bayer Prize. He has been Hinshelwood lecturer and Christensen fellow (Oxford 1988), was elected fellow of the American Physical Society in 1990 and later member of the Deutsche Akademie der Naturforscher Leopoldina (1998) and the Berlin Brandenburg (formerly Prussian) Academy of Sciences (1999). He is a member of the board of the Swiss Chemical Society as well as a member of several further scientific societies.

Motto: That everything changes is an unescapable fact which from time immemorial has moved poets, exercised metaphysicians and excited the curiosity of natural philosophers. Slow chemical transformations pursuing their hidden ways are responsible for corrosion and decay, for development, growth, and life. And their inner mechanisms are mysteries into which it is fascinating to inquire. (C.N. Hinshelwood [1])

1. Introduction

The occasion on which the Swiss Chemical Society has asked me to present this lecture is connected with the name of Paracelsus – a scientist born in Einsiedeln in 1493 and educated here at the University of Basel after 1510, who may be justly called one of the founders of the science of chemistry in the transition period from alchemy to chemistry, and a founder of the chemistry of life in the form of iatrochemistry or pharmaceutical or medicinal chemistry – greatly honors the work of my research group. It provides deep satisfaction and encouragement to me to know

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[#] Summary of the Paracelsus lecture held on Thursday 17 October 2002 on the occasion of the fall meeting of the Swiss Chemical Society during the r + d in life sciences fair, Basel that I have scientific colleagues and friends around who share the ideals of our research, as it was also always the greatest pleasure to have young coworkers with me who shared our scientific goals and efforts and without whom little of what I report below would exist as finished results.

Being selected to present this lecture is also a challenge in view of the group of previous Paracelsus lectures [2]. I shall resist the temptation here to connect this with a well-known joke about series of predecessors, recently retold in print [3], as I also shall resist the temptation to say more about Paracelsus (see [4], for instance), however, I shall mention some earlier Paracelsus lectures which have some scientific relationship to the present report. Otto Hahn's lecture [4] dealt with a connection of the fundamental physics of the nucleus with chemistry, a connection which shall be addressed from a current point of view in section 3. C.K. Ingold's lecture [5] dealt with organic reaction mechanisms and stereochemistry (see section 2 and 3), Manfred Eigen's lecture with his work on fast reactions [6][7] (see section 2), V. Prelog's work with organic stereochemistry [8], J.-M. Lehn's work with the role of intermolecular interactions in 'supramolecular' chemistry [9], (section 2), J.D. Dunitz's work relating crystallography transition states and reactions [10] (section 2) and finally Albert Eschenmoser's work with prebiotic chemistry [11] to which we relate in sections 3 and 4. It seems that the printed record of these lectures is not altogether complete. Given these historical connections to at least those authors mentioned above, the outline of the present lecture is briefly as follows.

In a first part (section 2) we shall provide some examples of our experimental spectroscopic approaches to fast molecular reaction dynamics and intramolecular processes (see also [12–21]). We shall briefly discuss here some recent results on tunneling hydrogen bond rearrangement and predissociation dynamics [22–26], fast entropy production in the quantum dynamics of femtosecond intramolecular vibrational redistribution in certain functional groups such as the alkyl CH-chromophore [19–21], and the stereomutation dynamics in ammonia isotopomers and other compounds in various limits of chiral symmetry breaking [14][15].

This leads us to the second part (section 3) on the recent theory of fundamental symmetry violations in chiral molecules and the new orders of magnitude discovered by us for parity violating energy differences between chiral molecules [27–33], which greatly change the outlook on the importance of this still very small effect in chemistry compared to results of earlier calculations [34–36].

In the third and last part of the lecture (section 4) we will address possible connections between the spectra and dynamics of chiral molecules with one of the most fundamental symmetries of physics (CPT [37][38]), looking at our current finding of predominantly matter (as opposed to antimatter) in the universe, our finding of predominantly L-amino-acids and D-sugars in the biopolymers of life on earth (as opposed to D-amino-acids and L-sugars) and our observation of time running uniquely in a forward direction in physical chemical processes (never really perfectly in the reverse way 'backwards') as possible 'fossils' of the evolution of the universe of life. Finally we shall conclude with a speculation on the irreversibility of molecular processes as related to possible molecular origins of thought [39].

In entering the details of our subject matter, we should perhaps provide some qualifications on the contents of the various parts. Even though theoretical analysis is an important part of our approach in section 2, the results on molecular processes presented (and referred to) therein are solidly based on *spectroscopic experiment*, a foundation which we consider to be among the most precise and reliable available in the physical-chemical sciences.

The second part (section 3) of our lecture dealing mostly with molecular parity violation is based on theory only. While we consider the underlying theory [27–33] now as well founded and quantitatively reliable, to the best of our knowledge, past experience teaches us that experimental check remains desirable and necessary, and it should become possible in the near future [32][33][40].

The third and last part of our lecture is largely based on speculation. Experimental and theoretical support or rejection may become available only in the more distant future, but it is possible, in principle, as we shall discuss.

2. From Molecular Spectra to Molecular Motion and Reaction Dynamics

2.1. *Brief History of Fundamental Ideas for Experiments in Chemical Kinetics*

Table 1 provides a greatly abbreviated history of the development of experimental ideas in quantitative 'fast' reaction kinetics, where what is fast depends on the time in history considered. The pioneer of quantitative chemical kinetics is clearly Ludwig Wilhelmy [41], who in the investigation on the 'inversion' of sugar in 1850 introduced time-dependent spectroscopic measurement by means of the study of the time-dependent optical activity of the solution containing sugar and acid. Secondly he introduced the quantitative time-dependent description by means of a differential equation for a (pseudo) first order rate law for the conversion of sugar (Z in the original) and its integration to exponential form with an effective rate constant k ($M \cdot S$ in the original), and finally implicitly introduced catalysis with the dependence of that rate constant upon the concentration of the acid (S in the original). Reaction times then could be easily measured by ordinary clocks. It took about half a century to clarify the role of reaction mechanisms composed of elementary reactions and properly define a composite reaction with its rate law following from the elementary steps, including a careful introduction of catalysis by Ostwald. In the period after 1900 the analysis of fast chemical reactions in terms of such elementary steps became a dominant theme of experimental research, with the need for ever faster measurements in order to properly isolate true elementary steps. As pioneers of this era we might mention Max Bodenstein and Cyril Hinshelwood among many others, later also B. Chance. It became clear that mixing of reactants would be a limiting step thus leading to the concept of 'immeasurably fast reactions', which were faster than any conceivable mixing scheme. The history of this has been lucidly told by Manfred Eigen [7], who introduced after 1950 in response to this difficulty the experimental concepts of relaxation techniques (such as T-jump techniques), where the mixing step is circumvented by a fast physical perturbation on a system initially in equilibrium, whose relaxation into the new equilibrium is then analyzed in terms of its reaction kinetics. In parallel to these developments the flash photolysis techniques, which used a photochemical perturbation, were introduced by Norrish and Porter (see [42]), including the idea of pump-probe experiments. Shock wave techniques were developed by a number of authors (see [18][43][44] and references cited therein). In the same period we find also developments which circumvent time-dependent measurements altogether by reducing the measurement of rates of bimolecular reactions to measuring cross sections in molecular beams, and the names of Taylor, Datz, Herschbach, Lee, Bernstein and Toennies might be recalled here (see [45][46] and references cited therein). For condensed phase reactions dynamic NMR spectroscopy with analysis by reduced density matrix Liouville techniques was developed in about the same period (see [47–50] and references cited therein). While molecular beam techniques [45][51–53] and other single collision experiments using quantum state preparation and detection with lasers [54–58] have contributed enormously to our understanding of bimolecular gas phase reactions, perhaps the most dramatic developments in terms of time scales in reaction kinetics came from the development of short pulse lasers and their use in pump-probe experiments [42][59–61], where the names of Rentzepis, Eisenthal and Kaiser may be named as representatives of the picosecond era following 1970 and Shank, Fleming, Hochstrasser, Zewail, Mathies, Laubereau, Zinth, Elsässer, and Keller for the femtosecond era following 1980 (see Table 1).

1. **After ~ 1850: Rate Constant**
(Ludwig Wilhelmy, Poggendorfs Ann. **81** (1850) 413, 499)
Quantitative time dependence
$$-\frac{dZ}{dt} = M_{konst} \cdot S_{äure} \cdot Z_{ucker}$$

2. **After ~ 1900: Reaction Mechanisms and Elementary Reactions**
increasing detail, complexity, sophistication
Mixing schemes: Faster, faster, faster …
„Immeasurably fast reactions“

3. **After ~ 1950: Don’t Mix at All!**
Relaxation techniques (T-jump …),
Flash Photolysis, Shock Waves
Chemical Exchange by NMR
(Condensed Phase Reduced Density Matrix Liouville Dynamics)
Molecular Beams

4. **After ~ 1960: LASER Pump-Probe Techniques**
Make Pulses Shorter, shorter, shorter…

→ ns	→ ps	→ x fs	→ 0 fs
>1960	>1970	>1980/90	1. April 90

5. **After ~ 1980: Don’t use pulsed pump-probe techniques at all!**
Intramolecular Dynamics from Quasi-Stationary High Resolution Spectroscopy (ns → fs → as)

Table 1. Brief history of fundamental ideas for experiments in chemical kinetics.

While a certain final point was reached with the report of the ‘0 fs pulse’ [62], we might mention here the most recent reports on time-resolved electronic processes in Kr atoms with 8 fs lifetimes and a claimed time resolution in the sub-fs (about 200 as) domain [63][64]. In mentioning here also a different type of ‘attosecond microscope’ developed for electronic processes in atoms, using relativistic heavy ions [65], we turn our attention now to a new experimental concept to derive molecular processes reaching the femtosecond, and if relevant the attosecond time domain, followed and developed systematically by our group in the years after 1980 (Table 1, point 5) (see [12][15][17–21] for some more detailed reviews of this).

2.2. *Quantum Chemical Kinetics in the Nanosecond to Attosecond Domain as Derived from High-resolution Molecular Spectroscopy Without Time-resolved Measurement*

The basic idea behind this experimental approach can be traced to the work of Schrödinger in the early days of quantum mechanics [66][67]: A careful analysis of molecular line spectra at high resolution should allow us to derive under certain constraints the molecular hamiltonian $\hat{H}$ governing the molecular dynamics under isolation, and if we include the analysis of line intensities also the hamiltonian $\hat{H}'$ including interaction with the radiation field [17][68]. Indeed, molecular spectra are usually analyzed in terms of time-independent stationary states, following the time-independent molecular Schrödinger equation (Eqn. (1))

$$\hat{H}\varphi_n(\{q_k\})=E_n\varphi_n(\{q_k\}) \qquad (1)$$

where the $\{q_k\}$ represent the set of all spin and space coordinates of all particles in the molecule, φ_n are the time-independent states depending only on these coordinates and not on time, with E_n the energy levels. The primary measurement concerns thus an energy measurement (strictly energy differences $E_n - E_m$) from spectroscopic line positions and when theoretical constraints on the molecular hamiltonian and line intensities are taken into account also φ_n. This is the bread and butter of all molecular spectroscopists. However, the same hamiltonian $\hat{H}$ governs also molecular time evolution by means of the time-dependent Schrödinger equation [66]

$$i\frac{h}{2\pi}\frac{\partial\Psi(\{q_k\},t)}{\partial t} = \hat{H}\,\Psi(\{q_k\},t) \qquad (2)$$

with the formal solution

$$\Psi(\{q_k\},t)=\hat{U}(t,t_0)\Psi(\{q_k\},t_0) \qquad (3)$$

and which would be valid both for $\hat{H}$ and $\hat{H}'$ (including external interactions), with a general time evolution operator ($\hat{U}$ and U'), which takes an especially simple form if we consider only $\hat{H}$ for the isolated molecule reaction dynamics

$$\hat{U}(t,t_0)= \exp[-2\pi i\hat{H}(t-t_0)/h] \qquad (4)$$

and which allows us to derive the molecular wavefunction $\Psi(\{q_k\},t)$ given an initial state $\Psi(\{q_k\},t_0)$ and the hamiltonian $\hat{H}$ from spectroscopy.

An even simpler understanding can be achieved from the general form of the solution of the time-dependent Schrödinger equation in terms of the stationary states φ_n in the case of an isolated molecule

$$\Psi(\{q_k\},t) = \sum_{n=0}^{\infty} c_n\varphi_n(\{q_k\})\exp(-2\pi i E_n t/h) \qquad (5)$$

with complex, time independent coefficients c_n determined by the initial state at $t = 0$.

While we have given here only the simplest presentation for the isolated molecule case and pure quantum mechanical states, the treatment can be generalized to interactions with external fields and to a statistical mechanical treatment of mixtures [17]. The in principle infinite sum in Eqn. (5), which is turned into an integral in the case of continuous spectra, is in practice experimentally truncated by the energy range covered by the spectra, which defines the effective time resolution Δt of the experimental approach by means of

$$\Delta t \geq \frac{1}{4\pi\Delta\nu} = \frac{1}{4\pi c\tilde{\nu}} = \frac{h}{4\pi\Delta E} \qquad (6)$$

Thus, if a rovibrational infrared spectrum has been analyzed (and fully understood in terms of $\hat{H}$) over a wavenumber range of $\Delta\tilde{\nu}$ = 15'000 cm^{-1}, which is realistic for experiments already carried out on some molecules [19][69–71], the corresponding time resolution would be somewhat better than about 200 as = 0.2 fs.

The above equations, which can be found even in initial textbook quantum mechanics, might generate somewhat too simple a picture of the process. Historically, there were several stumbling blocks in this development. The first was intellectual, as molecular spectroscopists over many decades restricted attention to time-independent analyses (Eqn. (1)) considering the time dependence either as absent or trivial (in the analyses of some ultrasimple processes connected to Lorentzian line widths or two level energy splittings). Neither of these intuitive assumptions is correct. Indeed, although time-dependent quantum mechanics in principle was largely understood from the work of Heisenberg and Schrödinger in 1925/26, in practice it remained a sleeping beauty in molecular reaction kinetics whose awakening may be related to the work on molecular electronic radiationless transitions by Jortner and his colleagues and further, related work (see [72][73], for instance). Another, highly nontrivial complication in the above analyses concerns usual spectroscopic analyses giving only immediate access to molecular 'spectroscopic constants' relating to *effective hamiltonians,* which do not directly provide access to the real hamiltonian $\hat{H}$ for a polyatomic molecule. The more recent history of this development has been told elsewhere [19].

Finally, the spectroscopic analysis leading to an adequate representation of the sum in Eqn. (5) needs the accumulation and analysis of a huge amount of spectroscopic information, which provides further experimental and theoretical difficulty. While some of this information is redundant when making appropriate model assumptions, the experimental requirements remain serious. On the other hand, and on the positive side for this approach, the actually very large amount of very precise experimental information from high-resolution molecular spectra provides frequently much more stringent constraints on an analysis than the usually more limited data from time-resolved kinetics, which in many cases can provide only very few significant parameters with rather limited numerical precision.

In addition to providing a new experimental approach, the spectroscopic quantum chemical kinetics also provides a fresh look at the theory of molecular reaction dynamics. In the past – and in today's textbooks – this is dominated by statistical mechanical or 'thermodynamical' quasiequilibrium theories such as Henry Eyring's transition state theory of thermal reactions or quaisequilibrium theory of mass spectra, 'RRKM theory' or the statistical adiabatic channel model [13][18][74][75]. These lead in their simpler forms to expressions for the quasiequilibrium rate constants in terms of transition state quantities marked by the famous special cross ‡, say for a unimolecular rate constant at temperature T

$$k(T)=\gamma\frac{kT}{h}\frac{Q^{\ddagger}}{Q}\exp(-E_0/kT) \qquad (7a)$$

$$k(T)\overset{def.}{=}\langle\gamma(T)\rangle\frac{kT}{h}\exp(-\Delta^{\ddagger}G^{\ominus}/RT) \qquad (7b)$$

or a specific unimolecular rate constant at energy E:

$$k(E)=\langle\gamma(E)\rangle\frac{W^{\ddagger}(E-E_0)}{h\rho(E)} \qquad (8)$$

We shall not discuss these equations in detail here (see [74][75], but note that rate processes are described here by purely static, quantum statistical quantities $W^{\ddagger}$ and $Q^{\ddagger}$, in essence. Some students may have wondered why Eyring chose that special cross. An answer is that under this cross at the saddle point or reaction barrier he buried all dynamics (Fig. 1). We shall discuss below the revival of real-time-dependent quantum molecular dynamics for two types of processes, where the failure of quasiequilibrium theories is most prominent

(i) Molecular tunneling reaction dynamics [15][24] and
(ii) Processes limited by the rate of intramolecular vibrational redistribution [14][19] [76][77].

We shall turn now to a brief discussion of current spectroscopic techniques in our group and then give a few examples of application. We might mention here also some pitfalls in the sometimes oversimplified presentation of the route from energy-resolved spectra to time-dependent dynamics: Neither the uncertainty relation $\Delta E\Delta t \geq h/4\pi$ nor the Fourier transform relationship between energy and time representation allows us to derive significant information on time-dependent molecular dynamics, in general (see [20] for a discussion of this point, which is very frequently misrepresented in 'elementary' discussions).

2.3. *Some Experimental Techniques for High-resolution Infrared Spectra*

The infrared range of the spectrum is most closely related to reaction dynamics in electronic ground states under ordinary conditions. There has been an enormous development of techniques in this range partly driven by the separate goal of im-

Fig. 1. Picture of Eyring's cross (slightly modified) at a mountain pass taken by R. Quack at Seiseralm in the fall of 2002. It is under this type of cross standing at a saddle point or mountain 'barrier' that Henry Eyring buried time-dependent molecular reaction dynamics.

proved spectroscopic analysis of trace gases in the atmosphere [78], but for our own work mostly driven by the need for better analysis of quantum chemical kinetics. Table 2 summarizes some developments in our laboratory. This Table collects some characteristic quantities defining the 'power' of a given spectroscopic tool. Besides the obvious quantities resolving power R_P and effective instrumental bandwidth δν we need to consider also the scanning range $\Delta\tilde{\nu}$ indicating over which range the techniques allow a molecular spectrum to be 'scanned' and the scanning power Δν/δν, which is a measure of the potential information content in a complete spectrum as scanned by this technique using its best resolution. The analytical sensitivity is related to the effective achievable absorption length L of direct absorption methods, or by other quantities, when indirect measures of photon absorption (such as ion current in resonantly enhanced multiphoton ionization REMPI) are important. The Table should help to free oneself from the notion that only one quantity – such as δν or R_p – defines the 'power' of a technique. One really needs to consider all those in Table 2 and in addition also further technical capabilities such as combination with supersonic jet techniques [19].

In considering Table 2 one clearly recognizes the outstanding scanning ranges of FTIR and ISOS/IRSIMS together with still good resolutions (the most recent Bruker prototype FTIR system built specially for the Zürich group and still singular worldwide achieves δν ≅ 20 MHz at a specified resolving power of $\cong 2 \times 10^6$ [79]. The former BOMEM prototype system at a somewhat lower resolution has a long record of development with supersonic jet techniques at high resolution in our laboratory [19]. ISOS/IRSIMS in addition to wide scanning range achieves high sensitivity in supersonic jets and in addition mass selection as a special feature [80][81]. Near infrared cw-diode laser cavity ring down supersonic jet spectroscopy, on the other hand, is a new development [82][83], which performs superbly by three of the four standards (except for $\Delta\tilde{\nu}$, where it is still quite good, and where we plan improvements in the future). It is not the place here to review these techniques in detail. But we note that it is the combination of these developments in our group which has allowed progress in the spectroscopic analysis of molecular kinetics. As noted in section 2.2. the achievable time resolution is defined by the scanning range $\Delta\tilde{\nu}$, but it is the resolution (δν) and effective sensitivity ('L'), which provides the basis for the necessary analyses of the spectra.

Powerful Spectroscopic Tools
→ to apply to Atmospheric Analysis and Quantum Chemical Kinetics

Measures of Power

1. Effective Absorption Length L
2. Resolving Power $RP = \frac{\nu}{\delta\nu}$
3. Effective Resolution (Instr. Bandwidth) δν
4. Scanning Power $SP = \frac{\Delta\nu}{\delta\nu}$
5. Effective Scanning Range $\Delta\tilde{\nu}$

	RP	SP	$\frac{\delta\nu}{\text{MHz}}$	$\frac{\Delta\tilde{\nu}}{\text{cm}^{-1}}$	$\frac{L}{\text{m}}$
FTIR	$\leq 2\times10^6$	$\sim 10^7$	20 – 70	20'000	100
Diode direct Abs.	$\gtrsim 2\times10^6$	$< 5\times10^4$	20 – 30	20 (2500)	100
NIR-Diode CW-CRD	$\gtrsim 2\times10^8$	$< 10^7$	~ 1	500	1000 – 10'000
ISOS/ IRSIMS	$\gtrsim 6\times10^5$	$\gtrsim$ 30'000 $(\geq 10^6)$	~ 500	500 (20'000)	(10^{-3}) Ion-detector

Table 2. Spectroscopic tools developed and used in the Zürich molecular kinetics and spectroscopy group.

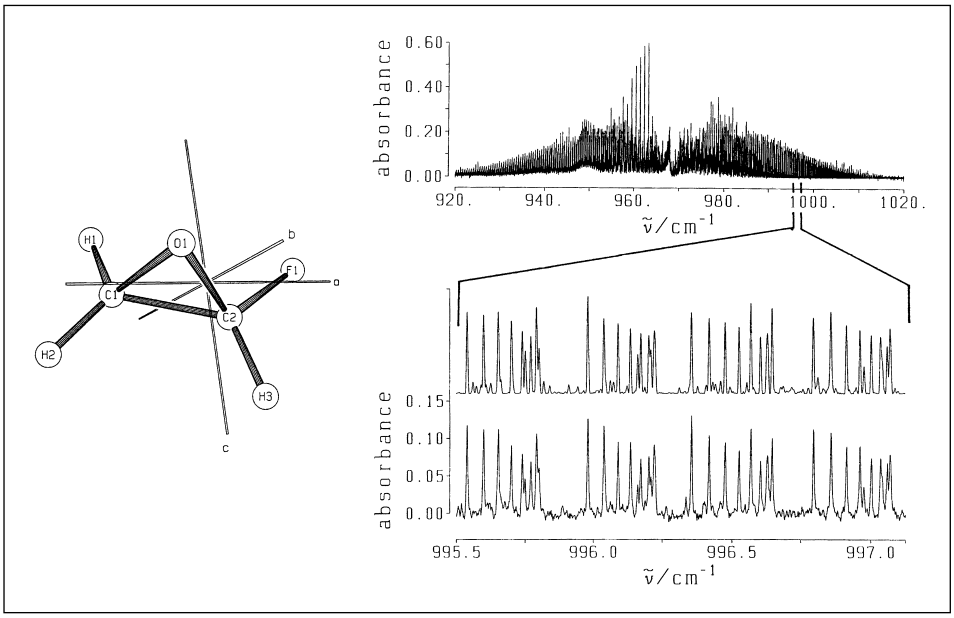


Fig. 2. FTIR Spectrum of fluorooxirane at room temperature (after ref. [84]). Because of the rigid structure of this chiral molecule with only relatively light atoms the spectrum could be analyzed without supersonic jet data (see simulation in upper part of lower panel).

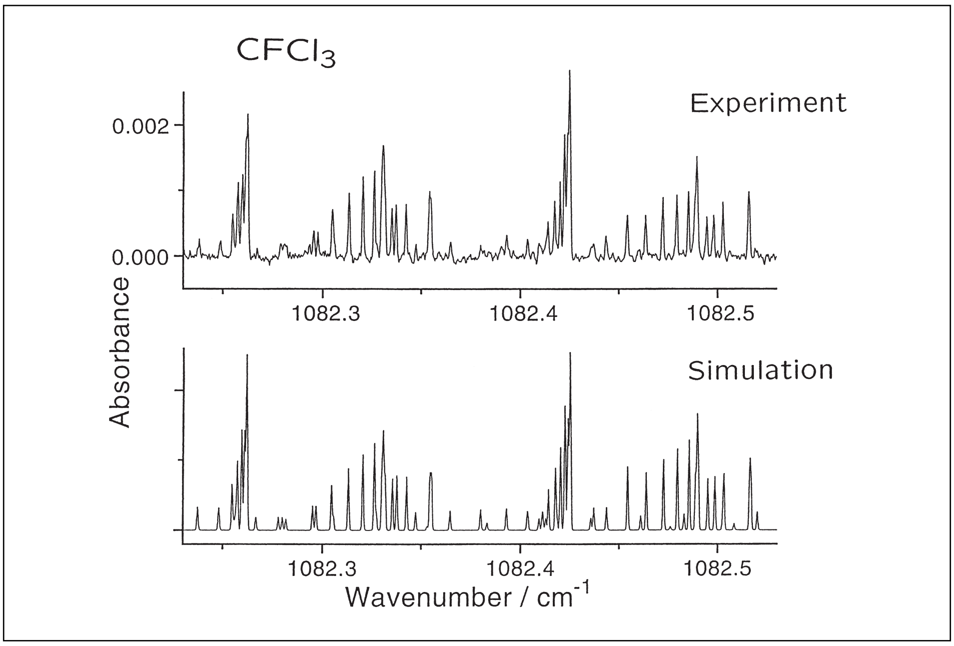


Fig. 3. IR-Diode laser spectrum of CFCl$_3$ taken in a supersonic jet expansion (after [85]) with an effective temperature T = 20 K. The room-temperature spectrum is too complex for analysis without prior data from supersonic jet spectroscopy.

We shall give here some examples of characteristic spectroscopic results from these techniques. Fig. 2 [84] shows a survey of one band and small section of this in a high-resolution FTIR spectrum of fluorooxirane, one of the very few examples worldwide still today where a high-resolution analysis of an infrared spectrum was achieved for a chiral molecule (all these examples were pioneered by the Zürich group) and which is relevant for our discussions in sections 3 and 4.

Fig. 3 shows a small section of the diode laser supersonic jet spectrum of CFCl$_3$ in the range of the 'atmospheric window', where we achieved an analysis after many years of effort by combining FTIR supersonic jet and direct diode laser absorption spectroscopy [85]. Here, the application of the spectra is in the field of atmospheric spectroscopy, and attempts of other laboratories in this rather vast research field to achieve such an analysis had failed for many years.

As a last example we show a measurement of isolated lines in the near infrared spectrum of methane by pulsed supersonic jet cw-diode laser cavity ring down spectroscopy in Fig. 4 [83]. Here the measurement of a single line P(1) at high precision together with the precisely known rotational levels in the vibrational ground state provides the term values for the rotationless (J = 0) vibrationally highly excited level $(\nu_2 + 2\nu_3)_0 = (7510.3378 \pm 0.001)$ cm^{-1}. This level F_1^- has well-defined (negative) parity and combines with nuclear spin $I = 1$ for the four protons and thus has a threefold degeneracy (total angular momentum $F = 1$ due to the spin [32]). In principle, there would be a hyperfine structure (F = 0, 1, 2 in the lower level with $J = 1$, $I = 1$). This is however not resolved for hydrogen, whereas with iodine substitution and for the iodine atom we have resolved even this using such techniques [86][87]. The Doppler line shape can be fitted (Fig. 4) providing an effective translational temperature of (53.7 ± 0.2) K in the jet. The effective resolution is determined here by the precision of the line center measurement close to about 10^7, fixing the upper level in the near infrared to within 0.001 cm^{-1}. The instrumental resolving power in principle would allow for $> 2 \times 10^8$ (see Table 2). After this precise single line center determination, which can

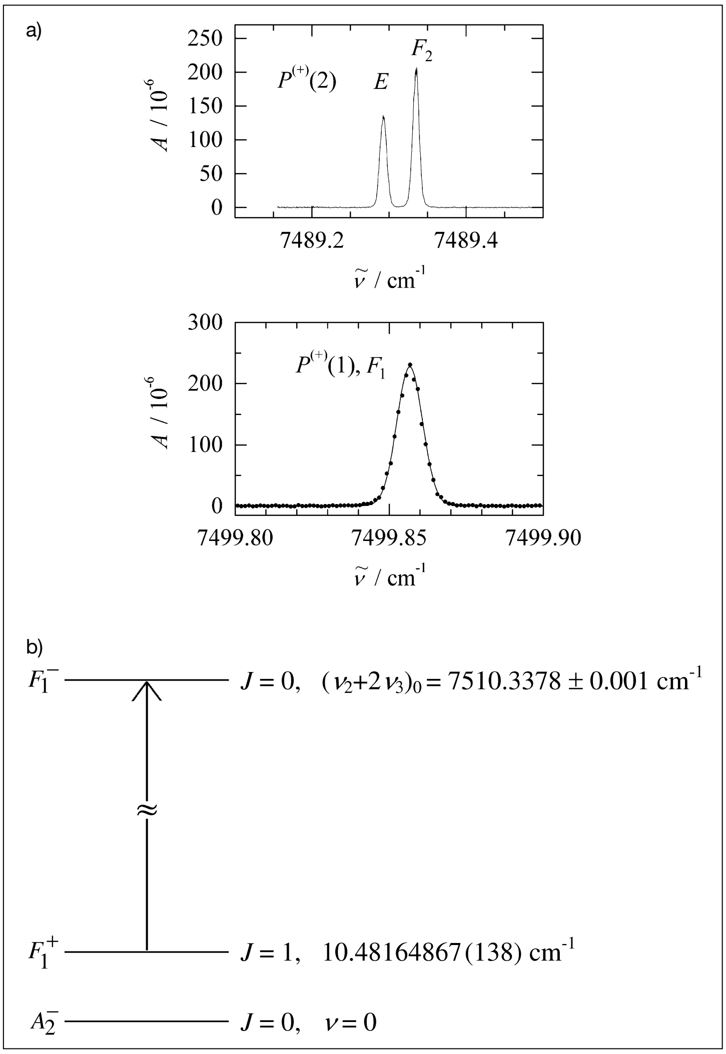


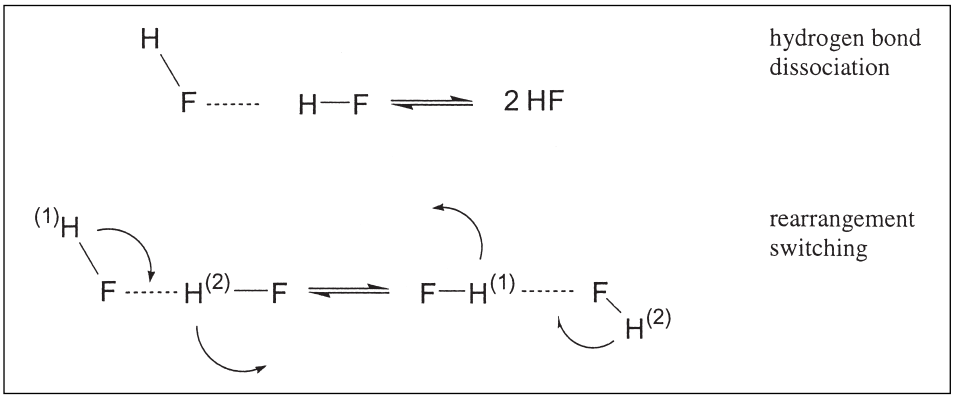
Fig. 4. Near infrared spectrum of methane measured by pulsed slit jet cw-near infrared laser cavity ring down spectroscopy. The upper panel shows the clearly resolved spectrum, including a Doppler shape analysis with T_{eff} = 53.7 (2) K for P(1), whereas the lower panel shows the level scheme for the P(1) transition including full symmetry assignments in the MS*$_4$ group [32].

be further related to vibrational dynamics and IVR [83], we shall now turn to more complex spectra of tunneling problems.

2.4. *Tunneling Reaction Dynamics and Predissociation in Hydrogen Fluoride Clusters $(HF)_n$*

We have used the pulsed slit jet cw-NIR-laser cavity ring down spectroscopy technique illustrated in Fig. 4 to study the near infrared vibrational, tunneling rotation spectrum of $(HF)_2$. A preliminary analysis had been achieved for this range by FTIR spectroscopy by us in 1989 [22], but only the recent experimental developments have allowed us to completely analyze these spectra. The long-term goal of the analysis of such spectra is a full quantum kinetic understanding of hydrogen bonded systems from the vapor to the condensed liquid and solid phases [22–25]. We shall discuss here a small section of this larger project. The Scheme shows the hydrogen bond dissociation and rearrangement processes. This type of kinetic process is of fundamental importance for understanding many kinds of hydrogen bond kinetics in hydrogen bonded liquids and in biomolecules with hydrogen bonds (for instance hydrogen bond breaking in the DNA double helix). The processes considered are based on tunneling dynamics and on–off resonant non-sequential or quasi-sequential intramolecular vibrational redistribution [12][22–25], and are highly non-statistical and mode-selective in complete contrast to traditional transition state, RRKM and related quasi-equilibrium theories of reaction kinetics.

For more details and general reviews of this important topic of hydrogen bond dynamics in $(HF)_n$ clusters we refer to [22–25][88]. We shall report here in some more detail on very recent results on the mode-selective hydrogen bond switching and hydrogen bond dissociation dynamics in the $(HF)_2$ complex in the energy region of the $N = 2$ polyad corresponding to excitation with two quanta of HF stretching between 7500 and 8000 cm^{-1}, exceeding more than seven times the dissociation threshold for breaking the hydrogen bond (1060 cm^{-1}). Loosely the two quanta of (HF) stretching can be distributed in three ways: (a) two quanta in the hydrogen bonded (HF) stretching mode, (b) two quanta in the 'free' non-hydrogen bonded (HF) stretching mode and (c) one quantum in each of the two modes. It turns out that these three different types of excitation lead to very different hydrogen bond dissociation and switching dynamics. While the detailed interpretation of these spectra and dynamics has been a long-standing question starting with early work in our group [22], a satisfactory experimental and theoretical solution has come about only very recently [26][89]. Table 3 summarizes these results.



Scheme. Predissociation and hydrogen bond switching rearrangement in $(HF)_2$.

N_j	(n_b, n_f)	$\hat{\nu}_0$ / cm^{-1}	τ_{PD}/ns	τ_{sw}/ns	τ_{sw}^{theory}/ns
2_1	(2,0)	7550.36	0.05	2.2	3.7
2_2	(0,2)	7682.82	1.1	0.16	0.16
2_3	(1,1)	7795.25	0.33	0.05	0.07

Table 3. Mode-selective tunneling switching and predissociation dynamics in the $N = 2$ polyad of $(HF)_2$. The first column gives the polyad level assignment (ordered by energy), the second column the approximate number of quanta in bonded (n_b) and in free (n_f) HF stretching modes, column three gives the band centers and the remaining columns the predissociation (PD) and switching (sw) times (after [26][89]). Theoretical results [89] are based on SO-3 surface [25].

2.5. *Tunneling and Stereomutation Dynamics in Various Limits of Symmetry Breaking*

A second large class of tunneling reactions concerns stereomutation in 'nonrigid' molecules [90–93]. The historical prototype is inversion in ammonia [93]. While in ordinary ammonia, interconversion does not exchange chemically distinguishable structures, it is nevertheless a particularly interesting system, which can be extended by appropriate substitution to, in principle, chiral amines [81]. Work in our group has aimed at systematically deriving the full quantum dynamics in ammonia isotopomers from systematic investigations of spectra and potential hypersurfaces [90–93]. As an example we mention stereomutation dynamics which was recently investigated with the aid of a full dimensional potential hypersurface for ammonia and tunneling quantum wavepacket calculations in a most relevant 4-dimensional subspace [91] of the NHD_2 isotopomer. Coherent infrared multiphoton excitation leads to energies substantially exceeding the barrier for stereomutation by inversion. Nevertheless, the inversion process remains essentially dominated by tunneling. While this molecular example has been under investigation for many decades, our quantum wavepacket dynamics provide completely new insights.

More generally, we consider tunneling stereomutation in chiral molecules. Fig. 5 represents schematically three different dynamical limits. The first case (A) concerns stereomutation in molecules with achiral equilibrium geometries. By distortion away from the equilibrium geometry one finds a chiral structure. Wavepacket evolution shows stereomutation between these achiral structures and racemization due to intramolecular vibrational redistribution. These phenomena have been studied for $CHDT_2$ and CHD_2T by extensive quantum dynamical wavepackets in appropriate subspaces drawn from a full 9-dimensional potential hypersurface [14][94][95]. We may talk here of dynamical chirality with 'zero' barrier for stereomutation [32].

The second type of system (B) has chiral equilibrium geometries but low barriers for stereomutation with large tunneling splittings. In these cases, enantiomers cannot be isolated as stable entities in 'bottles', but they can be generated for very short times and show stereomutation on the time scale of femtoseconds to picoseconds. Hydrogen peroxide [15][96][97] and aniline-NHD (C_6H_5NHD) are examples that we have studied [81][98]. These reaction systems have been analyzed with full dimensional quantum dynamical treatments either exactly (6-d for H_2O_2) or approximately (36-d for C_6H_5-NHD). We shall return to stereomutation in the case of stable chiral molecules (case C in Fig. 5) in section 3.

2.6. *Quantum Dynamics of Intramolecular Vibrational Redistribution (IVR) of Functional Groups in Organic Molecules*

The general question to be addressed here are the time-dependent primary kinetic processes of energy migration in polyatomic molecules. We have derived rates of such processes in extensive spectroscopic investigations over the last two decades. One finds very wide ranges of time scales from 10–50 fs for the fastest redistribution times in the alkyl CH chromophore to nanoseconds in the acetylenic CH, the NH, the OH, and HF chromophores under certain conditions. As we have reviewed this field on several occasions [12][14][19][21][77][99], we shall not discuss these in detail here but summarize only the outlook that arises from our findings of very mode- and group-specific redistribution times. On the one hand, this will have consequences for our future understanding of unimolecular reactions. Quasiequilibrium theories will have to be replaced by quantum kinetic theories taking the rates of energy redistribution into account explicitly. We have made a first step towards such theories already at the start of our investigations [76]. Secondly, our findings open many new possibilities to the so far elusive ‘mode-selective laser chemistry’ above and beyond isotope- and state-selective chemistry which all may well become routine techniques in the future, making use of our understanding of energy redistribution in molecules [17][20][100–102].

It may be instructive here to consider at least one of the more recent examples, in

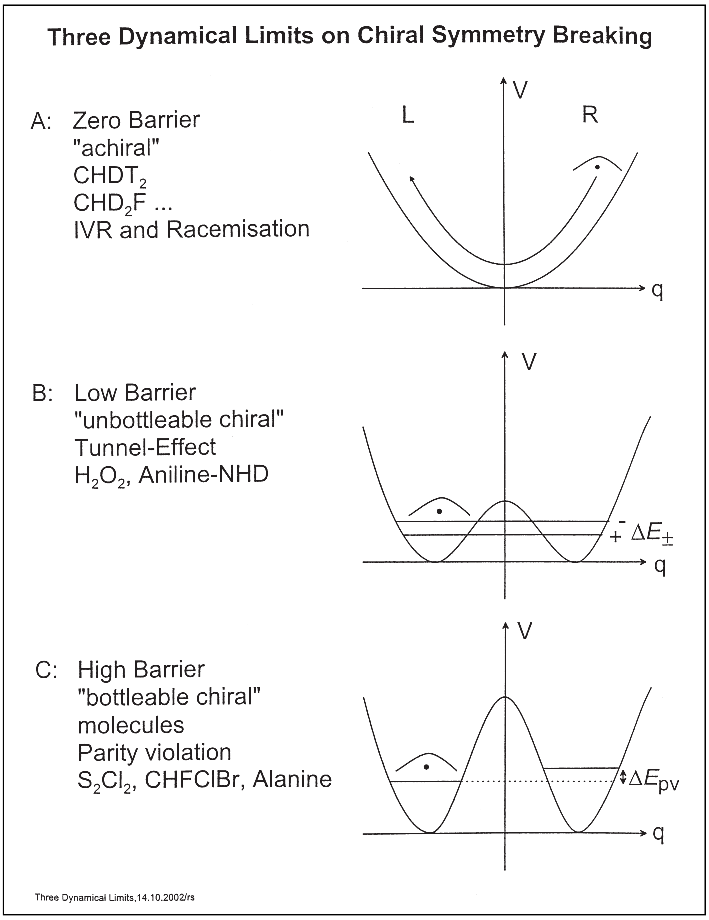


Fig. 5. Three dynamical limits of chiral symmetry breaking: A. concerns molecules that are achiral in their equilibrium geometry and become chiral by distortion, for instance due to coherent excitation [95]. B. concerns chiral molecules that have a chiral equilibrium geometry and fast stereomutation by tunneling [81][96–98]. C. concerns normal chiral molecules, where in fact parity violation dominates over tunneling [69–71][106].

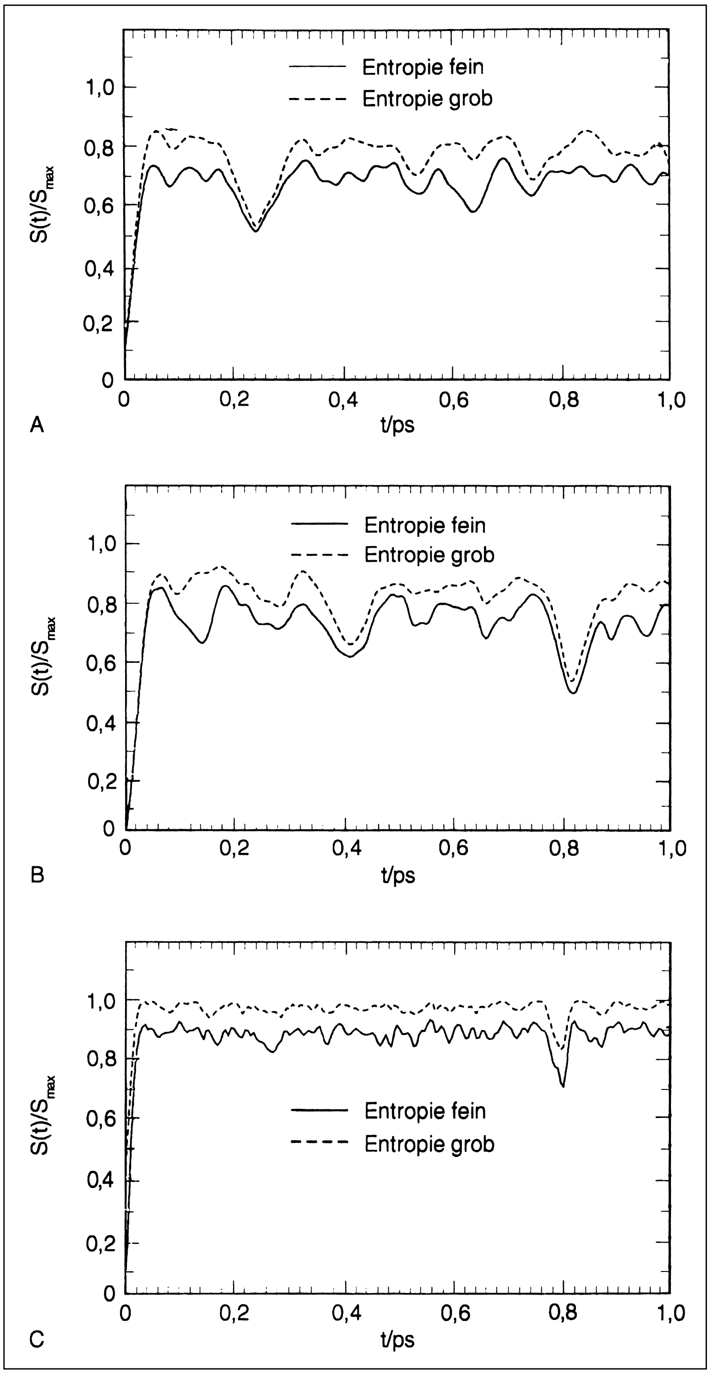


Fig. 6. Time-dependent micronanonical entropy production in a single isolated molecule of CHFClBr that is initially excited with 6 quanta of CH stretching (the results are from an analysis of high-resolution spectroscopic experiments [69–71], see also [38]).

which we choose entropy production after excitation with six quanta of CH stretching in the N = 6 polyad of CHFClBr [71] (Fig. 6). The initial time evolution shown in Fig. 6 in terms of the molecular entropy evolution can be considered to be a relaxation process with an entropy production $\mathrm{d}S/\mathrm{d}t \cong 5 \times 10^{14}$ $\mathrm{JK^{-1}mol^{-1}}$, which can be compared with typical values of 10^7 to 10^{12} for fast reactions and 3×10^{13} $\mathrm{JK^{-1}mol^{-1}}$ for typical vibrational relaxation processes in liquids. This very large entropy production could be made the basis of molecular machines, if coupled to appropriate processes. Independent of such speculative applications, it is of fundamental interest. Besides this broad view of relaxation and entropy production in isolated, single molecules, we draw attention also to the fundamental discovery of two types of intramolecular vibrational redistribution (IVR), the classical IVR, which roughly follows our classical picture of exchange of energy between otherwise separable oscillations in a chemical molecular structure, and quantum delocalization IVR, with loss of localized molecular structure during the IVR process [14][103][104].

We shall conclude here with a brief discussion of the time scales that we were concerned with here, to provide a rough order of magnitude overview [18]. Taking a typical age of a still young human being to be about 30 years or 10^9 s (about one human generation), then there are about as many nanoseconds in one second, as there are seconds or heartbeats in the time span of this one person or human generation. Furthermore, given the age of the universe around 13×10^9 years, there are in a rough order of magnitude somewhat fewer human generations in the whole lifetime of the universe, as there are nanoseconds in a second. Furthermore, if we take the attosecond as our ultimate time limit for electronic molecular and atomic processes then we find again this time factor of 10^9 in going from nanoseconds to attoseconds. High-resolution vacuum ultraviolet electronic spectroscopy is being developed and will open this time window in the future [105].

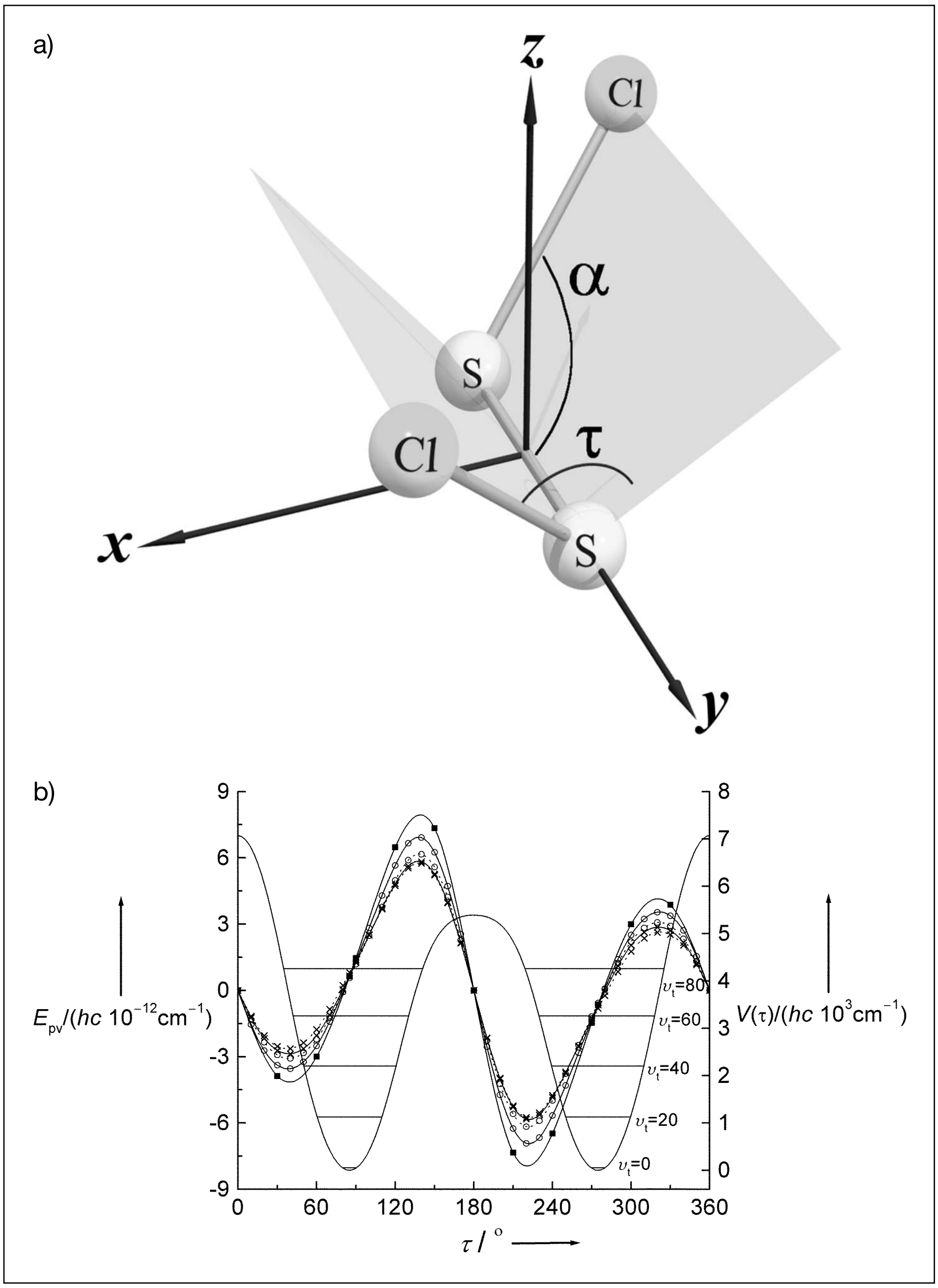


Fig. 7. Calculated torsional potential (full line, right ordinate scale) and parity violating potential (left ordinate scale, lines with various symbols for various approximations) for $\mathrm{Cl_2S_2}$, where the equilibrium structure and the definition of the torsional angle τ is shown in the upper part of the figure.

3. From Fundamental Symmetries of Physics to the Theory of Parity Violation in the Spectra and Dynamics of Chiral Molecules and its Role in the Origin of Life

Whereas the fast processes discussed in the previous chapter provide us with the rich possibilities of change in molecular kinetics, the fundamental symmetries of physics are at the origin of conserved quantities or constants of the motion, permanent and immutable for eternity [38]. However, small violations of these symmetries lead to slight disturbances in this static picture and introduce some fundamentally new possibilities for slow changes. We have recently reviewed several aspects of these phenomena in molecules and concentrate here on the three discrete symmetries C, P, T and their violations [32][33][38].

In traditional quantum molecular and particle physics it was assumed that the hamiltonian is invariant under the following operations

1. Inversion of all particle coordinates in the center of mass ('Parity' operation P or E*, which changes $x \rightarrow -x$, $y \rightarrow -y$, $z \rightarrow -z$)
2. Reversal of all momenta and spins of all particles ('time reversal' or T operation).
3. The exchange of all particles by their antiparticles (or operation C for 'charge conjugation').

We know today that these three symmetries taken individually are all inexact or 'violated' in elementary particle physics, while the combined (simultaneous) operation CPT is still assumed to be an exact symmetry in all of known physics [37].

Molecule [Ref.]	$\frac{\Delta E_{pv}}{(hc)\mathrm{cm}^{-1}}$	$\frac{\Delta t_{pv}}{\mathrm{s}}$	$\frac{\Delta E_{\pm}}{hc\,\mathrm{cm}^{-1}}$	$\frac{\tau}{s}$
H_2O_2 [27, 29, 96, 97]	4×10^{-14}	400	11	3×10^{-12}
D_2O_2 [29, 97]	4×10^{-14}	400	2	2×10^{-11}
HSOH [107]	4×10^{-13}	40	2×10^{-3}	16×10^{-9}
DSOD [107]	4×10^{-13}	40	1×10^{-5}	3×10^{-6}
TSOT [107]	4×10^{-13}	40	3×10^{-7}	0.1×10^{-3}
H_2S_2 [28, 108]	1×10^{-12}	16	2×10^{-6}	2×10^{-5}
D_2S_2 [108]	1×10^{-12}	16	5×10^{-10}	0.07
T_2S_2 [108]	1×10^{-12}	16	1×10^{-12}	33
S_2Cl_2 [106]	1×10^{-12}	16	$<< 10^{-70}$	$>> 10^{60}$

Table 4. Parity violating energy differences ΔE_{pv} and times (Δt_{pv}) for chiral molecules as well as tunneling splittings $\Delta E_{\pm}$ (and tunneling periods τ) for the symmetrical potentials (roughly rounded results[89] only for survey).

Of these three, parity violation has immediate consequences in molecular physics [33], the most striking being a prediction of a slight ground state energy difference of enantiomers corresponding to a nonzero reaction enthalpy for the stereomutation reaction

$$R \rightleftharpoons S \qquad \Delta_R H_0^{\ominus} = N_A \Delta_{pv} E \qquad (9)$$

Strictly speaking, this is true only in the dynamical limit (C) of Fig. 5, where tunneling becomes negligible. As the energies involved are exceedingly small, of the order of 10^{-11} Jmol^{-1} in typical cases [33], they have so far not been measured although schemes for such experiment have been proposed [32][33][40]. As we have discussed [33], such experiments in combination with accurate calculations could provide an alternative route to certain fundamental aspects of the 'standard model' of particle physics, complementary to the very costly and demanding experiments in high energy physics at CERN, Fermilab *etc.*

Until recently, there were actually also no cases known quantitatively, for which both the stereomutation tunneling splittings $\Delta E_{\pm}$ and parity violation had been calculated to demonstrate that Eqn. (9) would be valid with $\Delta_{\mathrm{pv}}E >> \Delta E_{\pm}$. Such a case has been recently studied theoretically in our group with the example dichlorodisulfane Cl_2S_2 [106]. Fig. 7 shows the equilibrium geometry calculated for this molecule together with the calculated torsional potential $V(\tau)$ for stereomutation as well as the parity violating potential E_{pv}. From this one sees two important facts. Firstly the torsional potential $V(\tau)$ is symmetrical with respect to the inversion point, whereas the parity violating potential E_{pv} is antisymmetrical. Secondly, the amplitudes of the two differ by about 15 orders of magnitude. We have calculated, that because of the high barrier of stereomutation (> 5'000 cm^{-1}) and the relatively heavy reduced mass for this motion, the tunneling splittings in the ground state for the hypothetical symmetrical potential would be about another 60 orders magnitude smaller. Thus it is theoretically calculated that the stereomutation dynamics of this molecule is in fact dominated by parity violation and $\Delta_{\mathrm{R}}H_0^{\ominus} = N_A\Delta_{pv}E$ would be about 1.4×10^{-11} Jmol^{-1} [106], in principle measurable by spectroscopic experiment on single, isolated molecules in a molecular beam, for example. Table 4 summarizes a series of molecules for which such calculations have been carried out which nicely show the transition between the cases of large tunneling splittings $\Delta E_{\pm} >> \Delta_{\mathrm{pv}}E$, where $\Delta_{\mathrm{R}}H_0^{\ominus}$ is not observable, and the opposite case $\Delta_{\mathrm{pv}}E >> \Delta E_{\pm}$, where $\Delta_{\mathrm{R}}H_0^{\ominus}$ becomes observable. Future experiments should provide such observations [33].

In a meeting under the general theme r+d in life sciences a few words should be said about the relevance of such calculations for our understanding of the origin of chiral selection of L-amino acids and D-sugars in the origin of life. Fundamentally this boils down to the very old question of a selection by chance (*de facto*) or by necessity (*de lege*), due to parity violation [27][32][33][38]. In spite of many discussions and repeated claims and proposals [109][110], we have pointed out in recent work and reviews [33][38][111] that the answer to this question is simply open today, and is likely to remain open for some time, in spite of the progress on parity violation reported above.

4. Speculations on CPT, the Origin of Matter and of Chirality in Life, the Molecular Origin of Irreversibility and of Thought

We live in a world of matter and not of antimatter, which occurs only in small amounts as an exception such as with positrons from β-decay. We find that the biopolymers of life are made of L-amino acids and D-sugars and not L-sugars and D-amino acids. Finally time seems to exclusively run forward, never exactly backwards. We have discussed elsewhere [38] that this observed apparent asymmetry can be related in a speculative way to CPT symmetry and its potential violation *de lege* at a fundamental level. It turns out that chiral molecules provide an ideal test of CPT symmetry [112]. Past tests of CPT symmetry have been concerned with comparing the mass of proton and antiproton, proving equivalence (and thus CPT symmetry) at a level of precision measured by $\Delta m/m \cong 10^{-9}$ [113]. It has been suggested to compare the optical spectrum of neutral hydrogen and antihydrogen atoms, providing a relative accuracy in the test of about $\Delta m/m \cong 10^{-18}$ [114], and recently larger amounts of neutral antihydrogen useful for spectroscopy have been produced [115], although optical spectra have not yet been measured. Our proposal [112] suggests to compare the spectra of $L(S)$ enantiomers of matter and $D^*(R^*)$ enantiomers of antimatter as described in the scheme of Fig. 8. With CPT symmetry the spectra would be identical and because of the close degeneracy of $L(S)$ and $R(D)$ enantiomers the spectra could be tested at an estimated accuracy of $\Delta m/m \cong 10^{-30}$ using the special technique suggested for parity violation tests in [40]. This would be by far the most sensitive test proposed for CPT symmetry. At the time we first suggested this and still today the realization of such an experiment might seem very remote, indeed. That would still seem so today, if we were proposing the synthesis of a chiral antimatter molecule of fluorooxirane or of CHFClBr. However, meanwhile, with large amounts of neutral antihydrogen being available, possibilities have much improved. Indeed we suggest here to produce potentially chiral clusters of the type $(H_2)_n$ or protonated (H_m^+) (of the type $[H_3^+(H_2)_n]$ *etc*), perhaps also negative ion clusters. Spectroscopic experiments on such chiral clusters and their antimatter equivalents following the scheme of Fig. 8 [112] would provide the type of information required. While this approach is still to be situated somewhat in the future, it is not as remote as it may have appeared a decade ago [112]. It may be noted that the structure of the larger clusters $(H_2)_n$ or (H_m^+) is not too well known, but it seems likely that some are chiral with a tunneling splitting satisfying $\Delta E_\pm << \Delta_{pv}E$.

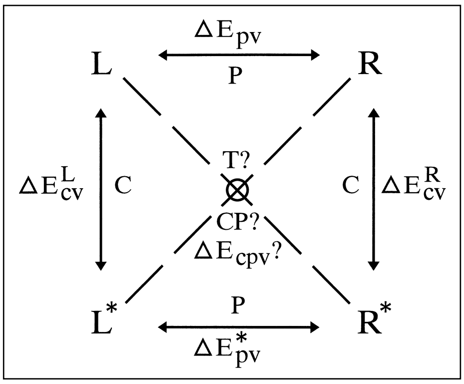
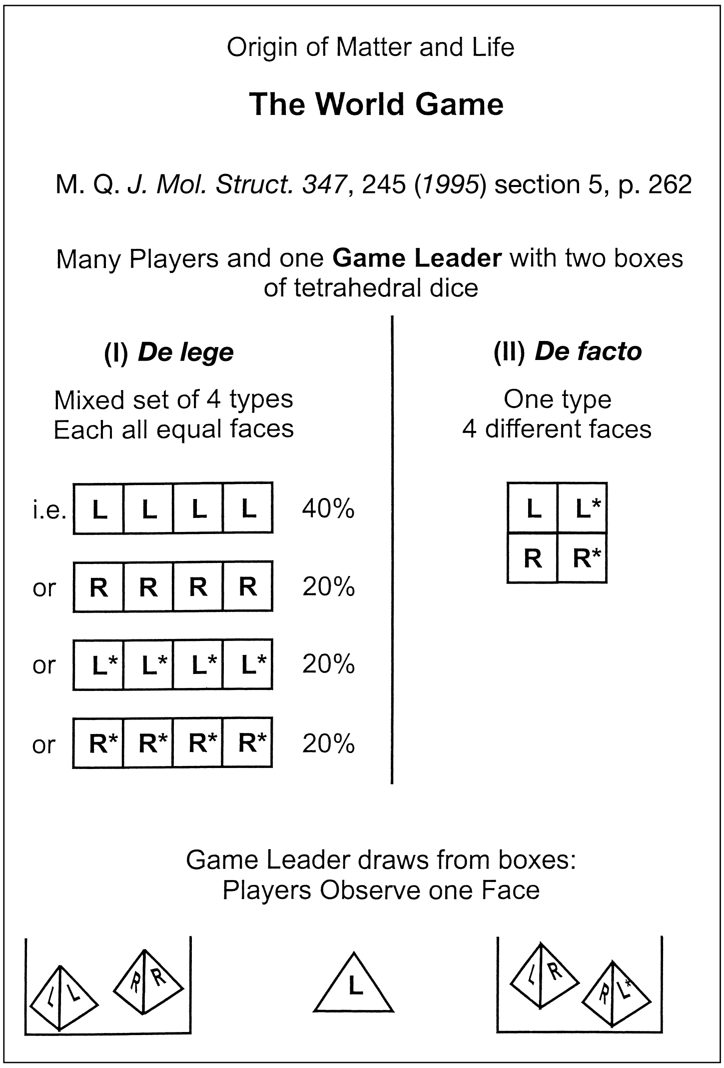


Fig. 8. Scheme of enantiomers (*L* and *R*) made of matter and antimatter (*L** and *R**, using a physicist's notation for enantiomers instead of *R*/*S* or D/L). With CPT symmetry *L* and *R** (and *L** and *R*) have the same energy and thus $|\Delta E^*_{pv}|=|\Delta E_{pv}|=|\Delta E^L_{cv}|=|\Delta E^R_{cv}|$. The experiment proposed in [112] would test for a deviation from these relations making use of the experimental principle proposed in [40] and thus testing the validity of CPT symmetry at about 10^{-30} relative precision.



Origin of Matter and Life

The World Game

M. Q. *J. Mol. Struct. 347*, 245 (*1995*) section 5, p. 262

Many Players and one **Game Leader** with two boxes of tetrahedral dice

(I) *De lege*

Mixed set of 4 types
Each all equal faces

i.e.	L	L	L	L	40%
or	R	R	R	R	20%
or	L*	L*	L*	L*	20%
or	R*	R*	R*	R*	20%

(II) *De facto*

One type
4 different faces

L	L*
R	R*

Game Leader draws from boxes:
Players Observe one Face

Fig. 9. The world game. The different types of dice used in the game are shown schematically with their four tetrahedral faces and the *de lege* box (bottom left) and the *de facto* box (bottom right). In the middle we show the single face allowed for observation, '*L*' in the example.

What would be the consequences if a tiny difference between spectra of *L* and *R** molecules or clusters were to be found in such experiments? The first consequence would be a complete revision or revolution of the standard model and in fact even all alternative current fundamental theories of microscopic physics. A second consequence would be the fundamental joint 'observability' of matter *vs* antimatter, left and right handedness of space and time directions forward and backward, which would not be granted with CPT symmetry being valid (see [38]), that is a very fundamental additional information about the structure of nature. It would also provide us with further insight in why it is that we observe the structure of the world in the way described at the beginning of this section. This can be illustrated by a game modestly called the 'world game' [21] in Fig. 9 and inspired by [116].

The world game is directed fundamentally towards the question of whether the current prevalence of matter over antimatter originating after the big bang and the prevalence of L-amino acids over D-amino acids originating in the evolution of life results from a 'chance' (*de facto*) or 'necessity' (*de lege*) symmetry breaking [21][38][112][117].

Citing from [21] the world game illustrated in Fig. 9 consists of a game leader who draws tetrahedral dice arbitrarily from two boxes shown at the bottom of Fig. 9, (I) the *de lege* box with four different types of dice each one having only one letter on all four faces, say *L*, or else *R*, or *L** or *R**, (II) the *de facto* box, where each die has four different faces (*L*, *R*, *L**, *R**). The players are allowed to make one throw with the selected die and observe the one face of the tetrahedron showing towards them. Then the players, who may be also called the 'scientists' must guess from which box the die has been drawn, that is 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 would be in science by the gain of insight). Now, if the *de lege* box has equal numbers of each die (*L*, *R*, *L**, *R**) and if the game leader is a statistically honest person, the statistics are fairly simple and the player does not have much of a winning strategy against the other players. If one player knows, however, that the *de lege* box contains a bias towards one type of die (say 40% *L*, and 20% of each of the others as indicated in Fig. 9), then he will win with the strategy of guessing '*de lege*' if he sees an *L* in a single throw, as shown at the bottom of Fig. 9 in the middle, and '*de facto*' if he sees any of the other faces. Indeed, however small the known bias is, he will always win in the long run over those who do not know the bias and that is why it is important to know the bias also in the analogous physical situation. In our world we observe living matter being made of biopolymers involving L-amino acids and of ordinary matter, for instance, and not of antimatter. The actually observed symmetry breaking in these terms is essentially 100%. However, this complete symmetry breaking relates to a relatively small thermodynamic bias, at room temperature perhaps with a ratio of the order of $(1 \pm 10^{-15}$ to $10^{-16})$, distinguishing L and D (*R*) amino acids, and in cosmology one estimates from the ratio of cosmic background photon to baryon numbers (10^9) a primordial bias of matter over antimatter with an initial ratio of $(1 + 10^{-9})$ after the big bang. Thus in both cases an almost complete selection results with a very small original underlying bias, leaving open here the detailed mechanisms of the selection. One obvious conclusion concerning the physical situation in biochemical evolution can be drawn from the single observation of an 'L-amino acid world': The bias cannot be 100% in favor of any combination of L^*, R, R^*.

After having thus ventured in cosmology, which for many is at the borderline between serious science, pure speculation, philosophy, or even worse, we shall cross that borderline – with appropriate warning – in conclusion of this lecture by a few cursory remarks on the molecular origin of thought and decision. One may wonder how a thought arises at the molecular kinetics level in the brain – if that is how it arises. The clearest crystallization of a human thought is a human decision, frequently assumed to be free, the famous '*homo viator in bivio*' or '*alea iacta*' (see Fig. 9). Let us assume that an 'elementary thought' at the origin of such a decision arises at the molecular level through a kinetic process in a single molecule, somewhat comparable to the elementary light signal observed in human vision arising through a photochemical *cis-trans* isomerization of a retinal molecule by absorption of a single photon and a long chain of subsequent events in the retina and finally the brain. We might call this the first hypothesis of 'molecular psychology'. Its understanding might be of importance in human life, although some might question, whether it can be made the subject of scientific, experimental and theoretical inquiry. We see no compelling reason why not.

Three related fundamental questions arise in this context from molecular dynamics . Firstly, is the 'molecular decision' reversible (related to time reversal and ultimately CPT symmetry), secondly is it repeatable and predictable, thirdly can it be influenced by an independent action of a separate phenomenon that we might call 'free will'? The first is related to the possibility of generating a time-reversed state and by two time reversals 'repeat history'. This would question the uniqueness of a historical event and decision. It is obvious that in ordinary mechanics such a uniqueness does not exist, but in real life it does. The symmetry breaking leading to this uniqueness could be *de lege* or *de facto*; we do not know the answer to this.

The question of predictability of the 'molecular decision' is related to the quantum uncertainty of molecular motion. We have shown elsewhere [38][39] that molecular dynamics is at a borderline of 'quasiharmonic' classical, and quantum dynamics and that depending on the type of molecule both practically predictable (in the deterministic quasiharmonic quasiclassical limit) and unpredictable dynamics (in the highly anharmonic quantum limit) can arise (closely related to CIVR and DIVR governed essentially by the anharmonicity of the underlying dynamics). One might speculate about nature's choice of the molecules of decision (if any) in evolution. Unpredictable dynamics based on quantum uncertainty can be made a physical basis for what we have called 'objective freedom of thought' (or will) [39]. The experimentally in principle testable existence of such a phenomenon would be consistent with our current understanding of quantum molecular physics.

The question of an 'extraphysical' psychological influence on the 'molecules of decision', which we might call 'subjective freedom of will or thought' [39] does not seem to be consistent with what we know at present about the laws of molecular quantum kinetics, in fact of all of microscopic physics. Nevertheless in our daily life most of us assume intuitively – and act on the hypothesis – that it exists. This is no proof, though, that is does.

5. Conclusion

We have started from the foundations of molecular kinetics solidly based on spectroscopic experiment , where some important questions have been answered during the last decades, but many exciting problems still exist. One direction of research here led us to fundamental symmetries of physics to be studied by the theory of quantum molecular kinetics and in the future by spectroscopic experiment. Sooner or later this will be successful. On the other hand, the questions on evolution, cosmology and 'molecular psychology' raised at the end of our lecture are likely to remain open for some time, although at least partially they might be made a subject of serious experimental research in the more distant future.

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