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Molecular quantum dynamics from high resolution spectroscopy and laser chemistry

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Intramolecular kinetics is of central importance as a primary process in chemical reaction dynamics in general and laser chemistry in particular. High resolution molecular spectroscopy provides one approach to studying the real time quantum dynamics of molecules. This paper outlines the conceptual background and briefly summarizes some results from the last decade with particular emphasis on recent work from our group in Zürich on intramolecular kinetics in the femtosecond to nanosecond domain. New quantum phenomena in intramolecular vibrational (rotational) redistribution (IVR) are identified, leading to two types of redistribution times, one quasiclassical, one purely quantal. The fundamental importance of symmetry and conservation laws — and their violation by weak forces of nature — for the primary processes of intramolecular kinetics is discussed.

1. INTRODUCTION: MOLECULAR SPECTRA, STRUCTURE, MOTION

The study of molecular spectra has a long and outstanding tradition as a means to derive information about *molecular structure* [1–4]. Spectroscopy has been extremely successful in providing data of very high precision on simple structural parameters such as bond lengths in diatomic molecules, data on "difficult species" such as free radicals or ions, or structural parameters of "difficult problems" in weakly bound molecules with highly anharmonic multidimensional motion such as the hydrogen bond molecule $(HF)_2$ [5]. X ray crystal structure analysis complements the spectroscopic approach to provide structural data for the highly complex macromolecules of biochemistry. Although, of course, many structural questions still remain open, including even some fundamental problems, in general our knowledge of molecular structure is quite satisfactory, as exemplified by the bond length data summarized in table 1, collected from [6] after 4 decades [1] of analysis. These bond lengths are defined as minima in the electronic potential functions for the center of mass distance of the nuclei or the HF monomer units in the case of $(HF)_2$. One may compare the accuracy in the bond lengths as given by the number of significant digits with the diameter of the Pb nucleus, for instance, which is about 0.014 pm, substantially more than the error in R_e, which is known with truly remarkable precision. For the hydrogen bond molecule $(HF)_2$ obtaining R_e from experimental data required the solution of the rovibrational Schrödinger equation using a highly anharmonic six-dimensional potential hypersurface, a

Table 1
Bond lengths in some diatomic molecules [6] and in the quasidiatomic hydrogen bond molecule $(HF)_2$ [5]

Molecule	R_e/pm
H_2	74.144
HF	91.680_8
HI	160.916
PbO	192.813
$(HF)_2$	271. ± 1

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structural problem that nowadays can be solved [5]. Much less indeed, is known about *molecular motion.*

Time dependent intramolecular dynamics is at the origin of the primary processes in chemical reaction kinetics [7–10]. Explicitly time dependent descriptions of intramolecular dynamics and chemical reaction dynamics arise naturally in classical mechanical trajectory calculations for the motion of the nuclei in polyatomic molecules, macromolecules or condensed phases [11–13]. A need for a detailed, explicitly time dependent quantum description arose particularly with the advent of coherent multiphoton excitation with various shaped pulses and observation on time scales from microseconds to femtoseconds [14,15]. The developments of short time laser experiments in the last decade [16–20] have generated an increasing interest in time dependent descriptions for these experiments but also more generally including time dependent scattering theory [21–29].

The experimental access to time dependent intramolecular dynamics is based on a variety of different approaches. While the field is still in its infancy, some most significant conclusions can be drawn from the work of the last decade. Table 2 presents a broad view of time scales of intramolecular primary processes. In the upper part of the table we show some physical primary processes ranging from elementary particles and cosmology to fast electron transfer and molecular vibrations. Of more direct relevance for chemical reactions are the redistribution processes shown in the lower part of the table (illustrated mostly with examples from our own work).

Nontrivial energy transfer processes between various vibrational motions have been characterized lately. These depend in specific ways upon certain structural features of molecules. About the fastest vibrational redistribution process identified so far is due to the Fermi resonance coupling between CH stretching and bending motions in the sp^3 alkyl CH-chromophore, combined with Darling-Dennison resonances between the bending modes in molecules that do not possess a threefold symmetry axis. Here we observe redistribution times of about 100 fs and even somewhat less, that is less than ten vibrational periods of the high frequency mode. More typical anharmonic redistribution times are from 1 to 10 ps, whereas adiabatic decoupling of high frequency modes from low frequency modes leads to much longer redistribution times up to a nanosecond and perhaps even longer. The slow relaxation processes after IR-multiphoton excitation of CF_3I observed by time resolved infrared spectroscopy on the nanosecond time scale may fall in this category, although other interpretations are possible [42]. Of course, efficient adiabatic decoupling is also known in many cases for the electronic degrees of freedom, where slow intramolecular electronic relaxation (internal conversion) is common, particularly when combined with the change of electronic spin state (intersystem crossing). The even weaker coupling between nuclear spin and other molecular degrees of freedom leads to a broad range of long relaxation times for change of nuclear spin symmetry by violation of the corresponding approximate conservation rule [35,36]. Finally very long times apply to the still unobserved, but theoretically predicted intramolecular relaxation of parity by means of the parity violating weak nuclear force and to the purely hypothetical violation of time reversal symmetry.

When discussing different *time scales for primary processes* due to different coupling mechanisms we should distinguish these from the great variation in *time scales in chemical reactions* arising from a combination of primary processes and merely statistical factors. An obvious example is the Arrhenius expression (1) for the rate constant of a thermal unimolecular reaction

$$k(T) = A(T) \exp(-E_a/RT) \qquad (1)$$

The exponential factor involving the Arrhenius activation energy E_a generates

Table 2
A Broad View of Time Scales for Primary Processes of Intramolecular Energy Transfer

Type of primary process	Time scale [reference]
a) Ultrafast primary processes	
Dynamics in the primordial, cosmic supermolecule	Planck time $t_P = \sqrt{(G \cdot hc^{-5})}$ $\approx 1.35 \times 10^{-43}\mathrm{s}$
Nucleon motion in nuclei	$t_n \simeq 10^{-20}\mathrm{s}$
Fast electron transfer and electronic relaxation	$t_e = h/E_h \simeq 1.52 \times 10^{-16}\mathrm{s}$
Nuclear vibrational motion in molecules ($\lesssim$ 3333 cm^{-1})	$t_v \gtrsim 10^{-14}\mathrm{s}$
b) Redistribution processes	
Strongly, preferentially coupled anharmonic	$t_{IVR} \gtrsim 100$ fs
vibrational modes (example CH-stretch bend resonances)	[24, 30, 31]
"Ordinarily" coupled modes	1 ps $\lesssim t_{IVR} \lesssim$ 10 ps
(example: CF_3 frame modes)	[9, 31, 43]
Adiabatically decoupled vibrational modes,	10 ps $\lesssim t_{IVRR} \lesssim$ 1 ns(?)
$\Delta\ell$ selection rule in rotation vibration coupling	
examples: —C≡C—H in acetylenes,	[32, 41]
HF stretching in $(HF)_2$	[33]
CF_3I (?)	[42]
Slower electronic relaxation of spin- or	$t_e \gtrsim$ 1 ns
adiabatically well decoupled states	[34]
Rotation — Vibration — Nuclear spin coupling;	1 ns $\lesssim t_{nsrv} \lesssim$ 1 s
Violation of nuclear spin symmetry conservation	[35, 36, 37]
Transfer of intramolecular parity	1 s $\lesssim t_{PV} \lesssim$ 1 day
(by violation of space inversion symmetry due to parity violating weak nuclear force)	[38, 39]
Violation of time reversal symmetry in molecular processes	? (>>1 day?, unknown [40])

almost any reaction time one could think of, from femtoseconds to the age of the universe. However, this arises from the statistical factors involving many activation steps, each of which being fast. The same is true for the power law for the threshold energy depedence of the chemical rate constant after multiphoton excitation

$$k(st,I) \simeq B\, I\, E_0^{-2.7} \tag{2}$$

In the linear regime,[8,9] each individual primary step in multiphoton excitation depends linearly upon radiation intensity I, but many steps are needed to overcome the threshold energy (energy barrier E_0), which results in an additional statistical factor, which is weaker here than in the other example. One may compare the relative effect of primary processes and statistical factors in chemical reactions to the escape rate of runners from a complicated forest. The individual speed of the runners corresponds to the rate of the primary process, which can be slower or faster (there are hares, hedgehogs and snails ...). The escape rate is secondly determined by the complexity of the path of the runners in the forest. For a complex "random" motion of the runners in the forest, the escape rate will be low, because of statistical factors. These statistical factors are reasonably well understood, whereas much less is known about the molecular primary quantum processes, on which we shall concentrate here. We note in passing, that "intelligent reaction control" generally will operate on the statistical factors ("by choosing an optimum path for the runners to increase the escape rate"). Less can be done about the primary processes, as they correspond to fundamental properties of the molecular hamiltonian (however some influence is also possible here with external fields). On various levels certain tunneling processes can lead to great varieties of time scales, which are not specifically indicated in the table.

Although not included in table 2 and not being the subject of this paper, the present introduction would be incomplete without mentioning the indirect kinetic evidence on intramolecular redistribution processes obtained by different versions of "collisional timing" using nonreactive gas colliders. These include the classic studies of Doering and coworkers [44] and Rabinovitch and coworkers [45] using chemical activation, the collisional quenching experiments of resonance fluorescence of benzene derivations of Parmenter and coworkers [46] and our work on the decomposition of isotopically labelled difluorobutanes after selective IR-multiphoton excitation [47]. The conclusion from these indirect studies has been that intramolecular vibrational redistribution in large molecules is completed after about 10 ps or less (see also [48–53]).

In summary of this introductory chapter we may say, that there is experimental evidence becoming available on rich structures for intramolecular rovibrational redistribution processes including slow and fast kinetics. A drawback of kinetic relaxation measurements — be it on the nanosecond or femtosecond time scales — and also of lineshape evaluations is the lack of detailed information about exactly what molecular kinetic processes are observed, i.e. one knows *how fast* they are but not *what* they are. For this, additional information is necessary, although this point is often overlooked. In the next chapter we shall summarize an approach, which we consider one of the most powerful available, although tedious.

2. MOLECULAR SPECTRA AND MOLECULAR MOTION

What are the primary processes of molecular motion during and after coherent excitation, for instance IR-multiphoton excitation? Answering this question in terms of molecular quantum dynamics implies studying wave packet dynamics or, more generally, with a statistical initial state, the probability distributions for electrons and nuclei in their multidimensional coordinate and spin space [15]. It seems unlikely, that observation of some time dependent absorption cross sections, Raman scattering cross sections, or of reactant and product concentrations even with so called state-to-state resolution will provide enough information to obtain the complete dynamics. We have therefore undertaken over the last decade or so an indirect, systematic approach towards polyatomic molecular quantum dynamics. It consists of a conceptually simple two step procedure:

(i) Obtain from high resolution spectroscopy and additional information (such as ab initio potentials in the adiabatic approximation) the molecular "spectroscopic" states (or "eigenstates"), their wavefunctions, transition moments, and the underlying molecular hamiltonian H ("potential surface" in Born-Oppenheimer language, but really more general).

(ii) Solve the time dependent equation of motion for the matrix representation **U** of the time evolution operator U in the basis of molecular eigenstates, possibly including coupling to a time dependent radiation field (say, from a laser).

To the extent that this program can be carried out accurately, this solves the molecular motional problem in its most general form. In practice, of course, there arise some problems in detail. We shall discuss some of the experimental and theoretical aspects of the major steps involved and then present a summary of selected results. Figure 1 presents a more detailed scheme of the approach.

Starting from high resolution molecular spectra in the upper part of the scheme the first step of traditional spectroscopic line-by-line analysis consists in a least squares adjustment resulting in the "best" spectroscopic parameters of an effective hamiltonian. One way to look at these parameters is to consider the analogy with the parameters of simple analytical term formulae (the diagonal part of the effective hamiltonian), being generalized to non diagonal matrix representation, with analytical formulae for off diagonal matrix elements as well. To avoid a common misunderstanding, we should stress that these spectroscopic constants of the effective hamiltonian do not correspond in a simple way to properties of the real molecular hamiltonian, for instance potential constants. If common analytical formulae for anharmonic constants from perturbation theory are used [54,55], the constants derived may be in error by a factor of two to five, as

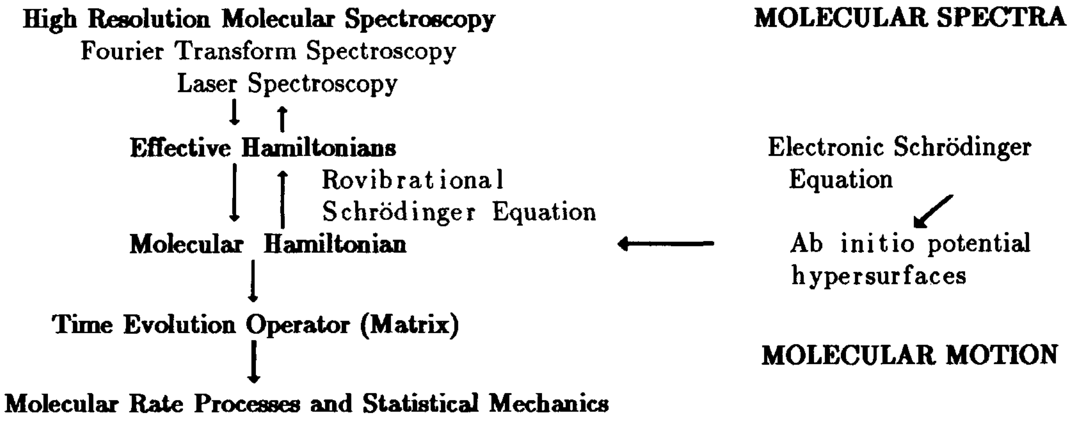

Figure 1 Scheme of the combined experimental-theoretical approach "Molecular Spectra and Molecular Motion"

has been demonstrated in a case study on anharmonic couplings in the CH chromophore [30,31,56]. Thus, the effective hamiltonian does neither directly provide the molecular potential function nor the molecular wavefunctions associated with the observed spectroscopic lines. Nevertheless, effective hamiltonians provide a compact representation of the spectrum and allow for predictions of unobserved lines. They can also be made the starting point for automatic assignment procedures [58,59]. The simple analytical structure of the effective hamiltonian may also contain fundamental insight, although in general the relation to the true molecular hamiltonian is complex.

The next step in the scheme is to derive the "true" molecular hamiltonian. This step is more complicated than commonly believed and generally cannot be carried out by means of spectroscopic, empirical information only. In practice, additional information is used, for instance ab initio calculations for some aspects of the potential hypersurface in conjunction with the Born-Oppenheimer (or adiabatic) approximations. Even then, the need arises to calculate molecular energy levels and wavefunctions by solving a multidimensional rovibrational Schrödinger equation for the polyatomic system

$$\hat{H}_{mol}\ \phi_k(r) = E_k\ \phi_k(r) \tag{3}$$

Here "r" designates the ensemble of all spin and space coordinates of all particles, in general, but for the rovibrational problem this is reduced to the space coordinates of the nuclei only. This still presents a formidable problem. Usually it is simplified by assuming either complete or adiabatic separability of some degrees of freedom from all the others. There is currently considerable activity in developing new methods in this field [57]). Table 3 A. summarizes methods used and developed in our laboratory in conjunction with the spectroscopic experiments (mostly FTIR-spectroscopy [31]). Usually, numerical solutions of the Schrödinger equation for an important subspace of the problem are combined with other vibrational-rotational motions by means of perturbation theory, separability assumptions etc. The number of dimensions treated numerically is shown for the examples (2-d, 3-d etc.). In the case of the Fermi resonance in CHX_3 symmetric top molecules the important part of the problem is 2-dimensional, for asymmetric tops CHX_2Y it is 3-dimensional. The straight-forward variational basis set expansion and grid techniques are generally limited to few dimensions. In contrast, Anderson [72] Quantum Monte Carlo techniques can be used for high dimensional systems and we have obtained accurate solutions for $(HF)_2$ with six vibrational and 3 rotational degrees of freedom. However, mostly ground states can be calculated in a direct way. For excited states additional approximations are necessary, such as the newly developed quasiadiabatic channel quantum Monte Carlo method [5,68,69]. There is little doubt that future developments will bring further progress. We shall turn now to the second step, the solution of the time dependent problem, assuming that the rovibronic, time independent problem has been solved by one of the techniques mentioned. This amounts to solving the differential equation for the time evolution matrix **U** in the basis ϕ_k of molecular eigenstates (rovibronic states)

$$i\frac{h}{2\pi}\frac{d\mathbf{U}}{dt} = \mathbf{H}(t)\ \mathbf{U} \tag{4}$$

In the basis of the molecular eigenstates and with a coupling to a periodic classical field, which is an excellent approximation to the laser fields in multiphoton excitation [14], one has explicitly

$$i\frac{d\mathbf{U}}{dt} = \{\mathbf{W}+\mathbf{V}\cos(\omega t+\eta)\}\ \mathbf{U} \tag{5}$$

with H_{mol} in the basis of eigenstates being diagonal

$$\mathbf{W} = 2\pi\ \mathbf{H}_{mol}/h \tag{6}$$

or

Table 3. Methods developed or used in the Zürich group (and some others) for solving the time independent and time dependent Schrödinger equations

A. Time independent problem (computation of H)

Method	Examples	References
Vibrational, variational, basis set expansion in normal or internal coordinates	2-d CHD_3,	56, 65, 66
	2-d CHF_3, $CHCl_3$, $CH(CF_3)_3$	60, 61, 62, 65, 66
	2-d $CHBr_3$, $CDCl_3$	61, 63, 64
Vibrational-rotational quantum Monte Carlo and quasiadiabatic channel quantum Monte Carlo	$(HF)_2$ (9-d, 6-d, 5-d + 1-d)	5, 67, 68, 69
	$(HF)_3$ (15-d)	68
Vibrational, numerical grid methods (3-d)	CHD_2F	70, 71
	$CHCl_3$ (isotopomers)	61

B. Time dependent problem of coherent radiative excitation (Computation of U)

Method	Typical Application	References
Direct numerical integration of differential equations	Ultrashort pulses, strong, nonperiodic fields	21, 22, 23, 24, 25
Floquet approximation (combined with numerical integration)	Typical, coherent laser pulses ps to μs periodic field	14, 15, 23, 24
Quasiresonant approximation (QRA) $H_{eff} \neq f(t)$	Typical laser pulses, not too strong coupling with near resonant states	14, 15, 73 80, 81, 82
Field free evolution similar	isolated molecules	30, 83-86, 89, 90
Closed analytical solutions	Degenerate levels	14
	harmonic oscillators	74, 75
Quantum statistical Master equations cases A, B, C, D	Very large numbers of irregularly coupled levels	14, 15, 76, 77, 79
Rate constants, first order kinetics	Typical laser pulses, only reaction rates needed	8, 9, 14, 15, 76, 77, 78, 87, 88

$$\hat{H}_{mol}\, \phi_k = \frac{h}{2\pi} W_{kk}\, \phi_k \qquad (7)$$

For electric dipole coupling (common in IR-multiphoton excitation) one has with z-polarized radiation (electric field E_0)

$$V_{kj} = -\langle \phi_k | \mu\, \mathbf{e}_z | \phi_j \rangle \left[\frac{2\pi}{h}\right] |E_0| \qquad (8)$$

μ is the electric dipole moment, $\mathbf{e}_z$ the unit vector in the z-direction. For other couplings this is to be replaced by analogous expressions. The function $E_0(t)$ designates the laser field amplitude, which is assumed to be slowly varying compared to the period of the field. With lasers in the mid- and near infrared the period of the field is in the femtosecond range (~ 30 fs for CO_2 laser), whereas variations in E_0 fall in the picosecond to nanosecond range, typically. $E_0 = 0$ corresponds to the special case of field free evolution of the molecules. One may thus assume that the problem can be decomposed into pieces with constant E_0 each. These pieces are joined smoothly to provide a laser field envelope function f, which varies slowly in time. If this is not the case, one cannot make use of the periodicity of the field, but then this is also not necessary. Because of the short times involved, one can then use one of the many schemes for direct numerical integration of the time-dependent coupled differential equations. In this case, the eigenstate expansion in our two step procedure is not necessary and may also not be the most useful starting point. It is a situation where radiative couplings are of similar strength as intramolecular couplings. While most recently a number of experiments fall in this class, it is not very common. It is often overlooked that direct integration methods will fail totally, numerically, when extended to "long" times into the picosecond and nanosecond domain of typical coherent laser excitation experiments.

For typical conditions of laser excitation in the longer time ranges, one may use the periodicity of the field by means of the Floquet-Liapounoff approximations [14]. If the coupling by the laser field is not too strong and if the importantly coupled states are fairly close to resonance at each step of coherent multiphoton excitation, one may use the quasiresonant approximation (QRA) [14], which only in the special case of the simple two level problem becomes identical to the well known rotating wave approximation (RWA). It is at the level of these approximations that the two step procedure with expansion of the time dependent problem in the basis of field free molecular eigenstates becomes essential. In this basis, it is possible to reduce the size of the basis, which for an exact solution would be infinite, to manageable numbers of coupled states. The quasiresonant approximation corresponds to a further transformation of this eigenstate basis to the quasiresonant basis [15]. We have critically discussed the merits of these techniques elsewhere [8,9]. Published program packages exist [73]. In very special cases, analytical solutions can be found [14,74,75].

The approaches discussed so far all attempt to solve the *complete* dynamical problem or statistical mechanical problem. In terms of the expansion in eigenstates we may write, using the $\mathbf{U}$ matrix from the solution of Eqs (4) and (5):

Solution of Schrödinger equation for the wavefunction $\Psi(t)$
(explicitly, with expansion in the eigenstate basis ϕ_k)

$$\Psi(t) = U(t,t_0)\Psi(t_0) \qquad (9a)$$

$$\Psi(t) = \sum_k b_k(t)\phi_k(r) \qquad (9b)$$

$$\mathbf{b}(t) = \mathbf{U}(t,t_0)\mathbf{b}(0) \qquad (9c)$$

Solution of the Heisenberg equations of motion for the observables Q (particle coordinates, spins and momenta, matrix representations $\mathbf{Q}$)

$$\mathbf{Q}(t) = \mathbf{U}^{\dagger}(t,t_0)\mathbf{Q}(t_0)\mathbf{U}(t,t_0) \qquad (10)$$

Solution of the Liouville–von Neumann equation for the complete density matrix P

$$P(t) = U(t,t_0)P(t_0)U^{\dagger}(t,t_0) \tag{11}$$

Even with the use of the QRA the ultimate problem in solving these equations is the size of the matrices, which would be of infinite order for an exact solution of real molecular problems. Good approximations require too large a basis to be tractable even for polyatomic molecules of modest size. One then may resort to statistical mechanical approximations. These can take the form of Bloch-type differential equations for *reduced density matrices ρ* for one mode or a subset of modes:

$$\frac{d\rho_{kk}}{dt} = f(\hat{H}, \rho_{jj}, T_1 ...) \tag{12a}$$

$$\frac{d\rho_{jk}}{dt} = f(\hat{H}, \rho_{lm}, T_2 ...) \tag{12b}$$

Alternatively, one can use Pauli-type master equations for average or coarse grained populations p_k of molecular levels (involving very large numbers of quantum states):

$$\dot{p} = Kp \tag{13}$$

One may connect Eqs (12) and (13). We think that future accurate treatments of time dependent quantum molecular dynamics will always be based upon such approaches for larger polyatomic and macromolecular systems. For a discussion of both fundamental and practical aspects we refer to [7–10,14,15]. At the final level of simplification of the dynamics one just calculates the generally time dependent reaction rate constant, as mentioned at the end of table 3. For thermal reactions, this will be the thermal rate coefficient, depending on T, P etc. For laser induced reactions it is the time- and intensity dependent reaction rate coefficient. Results on specific systems, in addition to those already mentioned in table 3, can be found in [80–91].

3. MODE SELECTIVE VIBRATIONAL REDISTRIBUTION AND LOSS OF MOLECULAR STRUCTURE: CLASSICAL AND QUANTUM REDISTRIBUTION TIMES (CIVR AND DIVR) AND IRREVERSIBILITY

The new spectroscopic approach to time dependent intramolecular quantum dynamics outlined in the previous chapter has led to numerous results for specific systems that are of considerable chemical interest. We wish to summarize here only three fundamental results of a general nature:

(i) We have established the *phenomenon of the group specific quantum dynamics of certain functional groups* (in the chemical sense) on the femtosecond to picosecond time scale [91]. Examples for this are the very distinct dynamics of the alkyl—R_3C—H, the aldehyde R—(C=O)—H and the acetylene R—C≡C—H. This group specific dynamics is semiquantitatively transferable for the same functional groups between different molecules and there exist as yet unexplored possibilities of its use in chemical and biochemical systems. In principle, this discovery opens up a totally new approach to chemistry.

(ii) We have established that *intramolecular vibrational redistribution (IVR)* occurs in a mode selective way. IVR for preferentially coupled modes occurs on the 100 fs time scale, whereas other modes may couple on much longer time scales of picoseconds and even nanoseconds. There exists a pronounced separation of time scales [83,92].

(iii) We have discovered a new type of quantum intramolecular vibrational redistribution beyond the well known quasiclassical redistribution of vibrational excitation between different vibrational modes. This new type of redistribution corresponds to a *relaxation process with loss of quasiclassical molecular structure* (in a certain sense) and has a relaxation time which may in general be very different from the quasiclassical redistribution time, depending in a critical way on the size of anharmonic couplings [24]. It may be worthwhile to explain this new phenomenon with a simple example. Consider two coupled vibrational modes. These may be, for instance, the CH stretching normal vibration in an alkane or other organic compound and the CH bending mode, or it may be an X-Y stretching mode and a Y-Z stretching mode in an X-Y-Z molecule, where Y may also be a more complex entity, not just an atom. We shall call the two modes "1" and "2" with coordinates "q_1" and "q_2". Classical mechanical or quasiclassical vibrational redistribution corresponds to an exchange of vibrational excitation between the two modes (by anharmonic coupling). If at time t=0 mode 1 shows a large amplitude of vibration, there will be a time at which the second mode 2 shows a large amplitude of vibration and we may call this time τ(IVR), the quasiclassical redistribution time, which in general will be large compared to the vibrational period of either mode ($\tau(\mathrm{IVR}) >> \tau(\nu_1)$ or $\tau(\nu_2)$). As time proceeds, vibrational exictation may return to mode 1 and so forth. Qualitatively the situation is well known from the case of two anharmonically coupled pendula in classical mechanics. In polyatomic molecules it occurs apparently at small anharmonicity and not too long times (but still $t >> \tau(\mathrm{IVR})$). If one mode is coupled to many, instead of the periodic exchange one has just relaxation. For this type of anharmonic motion at any given time the position of the atoms, that is "molecular structure", is well defined to within the limitations imposed by the uncertainty principle, which are not too stringent for moderately heavy nuclei (and even hydrogen). If this process, which we may now specify more closely as CIVR (with τ(CIVR)), prevails, we can use a classical picture of changing molecular structure during dynamics, as it would result from a classical trajectory calculation of molecular dynamics [11,12].

On very long time scales or if anharmonicity is very large (as in R_3CH), a new process becomes important. The probability distribution in the coordinates q_1 and q_2 ceases to be well localized but rather spreads or delocalizes on a time scale, which we may call τ(DIVR) (for **D**elocalization by **I**ntramolecular **V**ibrational **R**edistribution). If this happens, our concepts of well defined molecular structure, resulting from a narrow probability distribution for the positions of the heavy nuclei (or "atoms" cease to be adequate at times t such that $t >> \tau(\mathrm{DIVR})$. The quantum probability distribution in q_1 and q_2 becomes broad and we may call this also a loss of molecular structure (at least for the coordinates involved) by IVR. Such a phenomenon can only happen in the *quantum dynamics* of molecules but one may advance the hypothesis that it could be simulated by an ensemble of classical trajectories with a narrow distribution of initial conditions for the coordinates and fast spreading in the case of classical chaotic dynamics.

With this new phenomenon we can now distinguish two types of molecules or dynamical functional groups: for dynamically *quasiclassical molecules or groups* (C-type) we have

$$\tau(\mathrm{DIVR}) >> \tau(\mathrm{CIVR}) \tag{14}$$

For dynamically *nonclassical molecules or groups* (D-type) we have

$$\tau(\mathrm{DIVR}) \lesssim \tau(\mathrm{CIVR}) \tag{15}$$

The experimental data for R_3C—H and RXYC—H, for instance, show that the group specific CH stretch-bend dynamics belongs to the D-type to such an extent that the delocalization even approaches the statistical microcanonical equilibrium probability distribution for times of the order of a few hundred femtoseconds. The general observation and classification which we have put forward here will have fundamental implications for the understanding of unimolecular reaction dynamics and chemical reactivity, in general, that still have to be explored in more detail.

These observations also provide a new look at the physics of quantum irreversibility in complex quantum dynamical systems (such as polyatomic molecules). In order to illustrate and quantify this, we show in Fig. 2 the evolution of suitably defined quantum entropies for the subset of three strongly coupled CH modes in $CHClF_2$, initially excited with six quanta of pure CH stretching [90,91]. Within less that 100 fs 90% of the quasiequilibrium maximum entropy S_{max} for the subset of modes is attained, with subsequent fluctuations of an order of magnitude expected for such a small quantum system. The irreversible increase of entropy shown here for the quantum evolution of an isolated molecule is due to a *de facto* symmetry breaking of time reversal symmetry, as we shall discuss in the next chapter. The behaviour is qualitatively similar to the famous graphical illustration of the second law given by Boltzmann about 100 years ago in Vienna. If "at equilibrium" at 2ps we inverted all momenta, we would observe the time reversed mirror image of the evolution shown in the right hand part of the figure, with a return to zero entropy at t=0 (or t=4ps, if we continue to run time forward with a reversed initial state at 2ps. An interesting question arises concerning a possible violation of this time reversal symmetry in the real molecular evolution and we shall address this question now in a more general spectroscopic and kinetic context.

4. THE SYMMETRY OF TIME AND SPACE AND ITS VIOLATION IN MOLECULAR PROCESSES

The results reviewed in the previous chapters concern experimentally established facts of molecular quantum dynamics. We shall discuss now questions on molecular dynamics that we have addressed theoretically, but which still need experimental investigation in the future. These questions are related to the violation of fundamental symmetries of molecular dynamics as summarized by the invariances of the molecular hamiltonian with respect to [35,36]:

(i) any overall translation in space

(ii) any translation in time

(iii) any rotation of all particle coordinates in space

(iv) the reflection of all particle coordinates in the centre of mass (P or E*)

(v) time reversal or the reversal of particle momenta and spins (T)

(vi) any permutation of the indices of identical particles (nuclei and electrons)

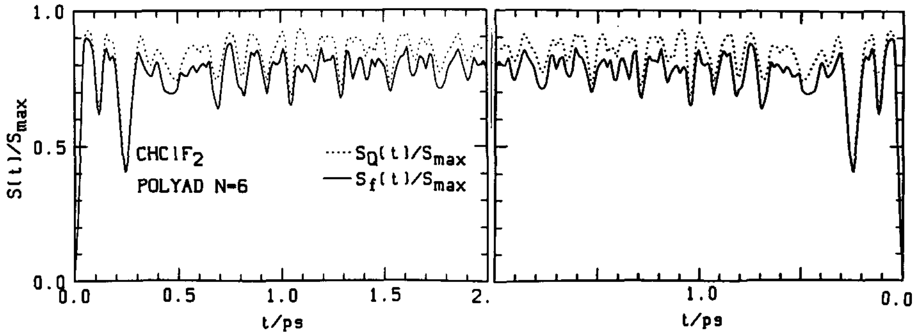

Figure 2 Quantum evolution of partial reduced entropy for the subset of strongly coupled CH modes in $CHClF_2$, with an inital state of six quanta of stretching from t=0 to t=2 ps and the mirror image evolution, formally from t=2 ps backwards to t=0 ps as forward process (see discussion in the text and [90,91]).

The list could by complemented by (vii) charge conjugation symmetry (C) if we included consideration of antimatter.

These form the symmetry group of the molecular hamiltonian. The first three operations are continuous and lead to conservation of (i) momentum, (ii) energy and (iii) angular momentum. The final three are discrete and lead to (iv) parity conservation, (v) time reversal symmetry of molecular motion and the last symmetry (vi) results in the generalized Pauli principle. Until now, no serious experimental evidence whatsoever has been put forward concerning a violation of the three *continuous* symmetries and their conservation laws. On the other hand, in the range of *discrete* symmetries parity violation is well known in nuclear and particle physics, although not yet established in molecular physics [39]. There is indirect evidence concerning the violation of time reversal symmetry in the single case of the CP violating decay of the neutral K^0 meson [40,93] and one might speculate about violations of the generalized Pauli principle [94,95].

The two discrete symmetries of space inversion (iv) and time reversal (v) are closely connected and of particular current interest, as the observation of their violation might be in reach for experimental molecular physics by spectroscopic and kinetic techniques related to those discussed above. After all, we would be hunting again for the true molecular hamiltonian in the scheme of Fig. 1, but now for very small asymmetries, *inconsistent* with the list of invariances given above. The two symmetries of particular concern may be called the symmetries of time and of space, and their violation will lead to asymmetric time and space as we shall discuss now. In the chemists everyday life we may talk specifically about:

1. The mirror symmetry of space, i.e. the left-right symmetry leading to the (alleged) energetic equivalence of enantiomers for chiral molecules.
2. The reversibility of molecular, dynamical processes.

Interestingly, both symmetries are heavily violated in practice. In biochemistry only *one* set of chiral aminoacids or sugars is important. Furthermore, ordinary processes of chemical kinetics are irreversible. We have shown [40] that the origin of these asymmetries is not well understood, because in each case at least two contradictory explanations can be given for the asymmetries, which could be, but have not yet been subjected to experimental test. We shall address the conceptual background and experimental situation first with the case of chiral molecules, which is most easily visualized.

4.1. The symmetry of space and molecular chirality

Because of the underlying relativistic connection of the three space coordinates x, y, z with the time coordinate (of the dimension of length in the product ct), a fundamental discussion might start from a reflection of coordinates at the origin ($x = y = z = ct = 0$) of this four dimensional space. However, the chemist's intuition is more easily attracted to the mirror symmetry of space alone. This symmetry and its violation appear prominently in *chiral molecules*, with which we can illustrate some fundamental concepts of symmetry breaking most easily, at a relatively elementary level. Fig. 3 demonstrates molecular chirality with the example of a substituted methane derivative.

By definition the two *enantiomers* shown are related as an image and its mirror image as are idealized left and right hand, which is at the origin of the terminology (from greek $\chi\epsilon\iota\rho$, hand). If we carry out the mathematical operation of inversion of the coordinates at the origin ($x \rightarrow -x$, $y \rightarrow -y$, $z \rightarrow -z$), we formally transform one enantiomer into the other, as one can easily see by inspection of the figure. This corresponds to a change from a left handed to a right handed coordinate system. If

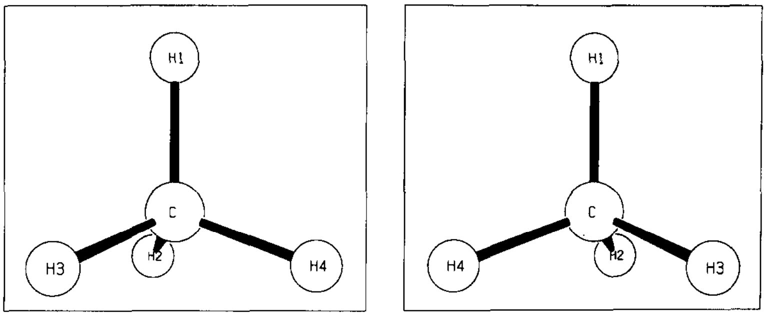

Figure 3 Chiral methane derivative and its mirror image (with four different subsituents, which can be the four "hydrogen isotopes" H1 = H, H2 = D, H3 = T, H4 = Mu, Myonium or four inorganic substituents H, F, Cl, Br or four organic sbustituents, for instance in amino acids of the D- and L-series). The two enantiomers cannot be transformed into each other by a rotation in space, but by an inversion at the carbon atom, which needs a large activation energy. Methanes with four "identical" hydrogen substituents (all protons e.g.) could be chiral by parity violation or violation of the Pauli principle [39,40, section 4.5.].

physical phenomena are invariant under this inversion operation, we can talk about the corresponding symmetry of the physical space in question (the ordinary "mathematical" cartesian space obviously shows such a symmetry).

The methane derivatives in fig. 3 have a well known biochemical and historical significance. Setting H1 = COOH, H2 = R, H3 = NH_2 and H4 = H one obtains the amino acids (left the "L-series", right the "D-series" in conventional nomenclature, e.g. with R = CH_3: Alanine, R = CH_2OH: Serine, R = $-CH_2COOH$: Aspartate, R = CH_2CONH_2: Asparagine). Ordinary biochemistry uses only the L-amino acids in proteins. However, both D- and L-amino acids are stable, easily prepared and distinguishable by simple tests (for instance by optical rotation of the plane of linearly polarized light by these "optically active" substances, or even by their taste: S-asparagine tastes bitter, R-asparagine tastes sweet). If not all of the substituents are different, for instance all equal as in methane, then the molecules in fig. 3 are chemically identical (and not optically active). The "simplest" substitution at C leading to a potentially chiral molecule would be with the four hydrogen isotopes as indicated. Of course, tritium (T, half life twelve years) and Myonium (Mu $=\mu^+e^-$, life time 2.2 μs) are unstable and hence CHDTMu would be highly radioactive, if prepared. It might be detected as a short lived species by the characteristic C—Mu stretching fundamental absorption, predicted here to occur around 9000 cm^{-1} in the near infrared. Other isotopomers of methane, such as CH_2D_2 are by ordinary standards achiral. Assuming mirror symmetry of space, even the optically active enantiomers are energetically and thermodynamically exactly equivalent in the sense that they have the same energy and entropy at all temperatures (including T =0 K). Nevertheless, it is a biochemically well established fact that *at least by history of evolution* the D and L series are not equivalent. We shall now discuss the two most important independent (and as explanations contradictory) types of symmetry breaking that may be at the origin of chirality (and possibly asymmetry of space, for a more complete discussion see [39,40]).

4.2. Symmetry breaking de facto and de lege

For visualization we shall discuss the fundamental concepts of symmetry breaking by means of a simple mechanical model of chiral molecules. The underlying physics is, of course, independent of the model used for illustration.

(i) De facto symmetry breaking as concept in classical mechanics. This interpretation of molecular chirality goes back to van't Hoff [96]. The two stable enantiomers of fig. 3 can be viewed as minima in a symmetrical potential as shown in figure 4. In the molecular model of fig. 3 one can take as characteristic coordinate q for the potential function the torsion of pairs of substituents H1, H2 and H3, H4 with respect to each other, with a maximum in the planar structure. The optimum reaction coordinate for inversion will in general be more complicated with a less symmetric transition structure [97]. Our one-dimensional model corresponds to the motion of a mass point in a symmetrical potential as shown in fig. 4 (lower part). For the position of the mass point we have three equilibria (with $dV/dq = 0$), two stable ones, corresponding to the left and right minima (physically the enantiomers) and an unstable one, which corresponds to the symmetrical achiral structure at q_C with a local maximum in V. We have *de facto* symmetry breaking in this potential if we choose at low energy the initial condition such, that the mass point is localized *either* at the left hand side *or* at the right hand side (and in classical mechanics *there is no third possibility*). The mass point may carry out small vibrations around either minimum. The actual position of the mass point (left or right) allows no conclusions about a possible asymmetry of the potential. However, if the potential is symmetrical, then the two possible asymmetrical states are symmetrically equivalent, energetically. However, at low energy, a symmetrical state is impossible.

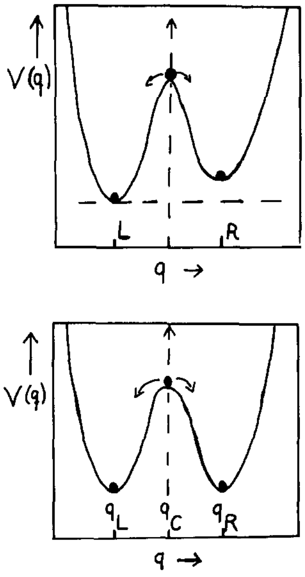

Figure 4 Potential function for the classical mechanical motion of a mass point in a symmetrical potential V(q) (one dimensional model of mirror symmetry of space with origin at qc) or in an asymmetrical potential V(q) ("asymmetric space") illustrating de facto and de lege symmetry breaking.

(ii) De facto symmetry breaking as quantum mechanical concept. This interpretation of molecular chirality is due to F. Hund [98] and results from the quantum mechanical treatment of the mass point in the symmetrical potential in fig. 4. The solution of the quantum mechanical equations of motion leads now to a probability distribution for the position q of the mass point. This is shown in figure 5. The lowest "stable", time independent wave functions correspond to χ_+ and χ_-. The absolute square of these corresponds to a probability distribution which is symmetric with respect to reflection at q_C. These states have well defined parity (+ and −) and are thus by symmetry achiral (for a potentially chiral molecule). We have, however, the freedom to choose the initial conditions corresponding to a chiral structure, with wavefunctions

$$\text{"left"} \qquad \lambda = \frac{1}{\sqrt{2}}(\chi_+ - \chi_-) \qquad (16)$$

"right" $$\rho = \frac{1}{\sqrt{2}}(\chi_+ + \chi_-) \qquad (17)$$

These states do not show the symmetry of the hamiltonian, but are chiral, the symmetry being broken *de facto* by the initial condition as in the case of classical mechanics. However, in quantum mechanics several new aspects arise. The states λ and ρ are not completely stable at potential minima but have a finite energy at which they interconvert by the tunnel effect. The rate of interconversion is very slow, if the reduced mass is large and if the potential has a high maximum and large width for the barrier in the middle. The time for interconversion can be calculated from the energy difference $\Delta E_\pm$ of the states χ_+ and χ_-

$$t(\lambda \to \rho) = \frac{1}{2}\tau_{\lambda\rho} = \frac{1}{2}\frac{h}{\Delta E_\pm} \qquad (18)$$

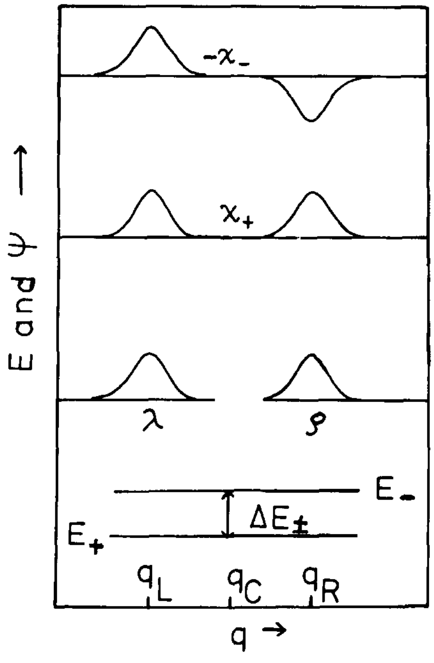

Figure 5. Quantum mechanical energy levels (E) and wavefunctions ψ (λ, ρ, $\chi_\pm$) for the case of a symmetric potential with de facto symmetry breaking.

Already the very rough estimates by Hund [98] gave interconversion times of millions of years if one inserts potential parameters corresponding to typical chiral molecules with stable enantiomers. From a practical point of view the symmetry breaking *de facto* is thus similar in classical and quantum mechanics.

However, the second and fundamentally new aspect in quantum mechanics is the *existence of a third possibility* of achiral states with well defined parity, which in a sense are as well left handed (λ) as they are right handed (ρ):

$$\chi_+ = \frac{1}{\sqrt{2}}(\lambda + \rho) \qquad (19)$$

$$-\chi_- = \frac{1}{\sqrt{2}}(\lambda - \rho) \qquad (20)$$

If we measure the structure of molecules in the state χ (for instance +), we find with equal probability both enantiomers. It would be wrong, however, to call this an ordinary mixture of enantiomers, but rather each χ must be considered a *"pure, achiral isomer"*, if we use the term pure isomer for the pure quantum state. We mention here the formal relation of these delocalized quantum states to the delocalized states mentioned in section 3. The nonclassical phenomenon is a direct (and here simple) consequence of the quantum mechanical superposition principle. One chemical consequence is that we may consider a racemic mixture with equal right to be either a mixture of chiral molecules of R(ρ) and S(λ) structures or to be a mixture of achiral molecules with positive (+) or negative (–) parity, the second being less familiar to the chemist. In a paper being presented in Vienna it would be appropriate to admit here, that experimentally the *"third possibility"* of well defined parity (+ or –) has so far not been realized and thus seems as hidden as the well known *"third man"*, but we have little doubt [38–40] that both will appear at a later stage of our story. (A certain type of spontaenous symmetry breaking by a superselection rule would exclude the third possibility [99]).

(iii) De lege symmetry breaking by the parity violating weak nuclear interaction. This type of symmetry breaking is often called *symmetry violation* in the more restricted, technical sense. It is illustrated with the asymmetric potential in figure 4 for the model of the mass point (the asymmetry being greatly overemphasized). In chiral molecules such an asymmetry in the effective potential is induced by the parity violating weak nuclear interaction and can be estimated to be of the order of 10^{-14} J mol^{-1}. This can be compared to potential barriers of the order of 2×10^5 J mol^{-1}, 20 orders of magnitude larger. It is certainly justified to talk about a small symmetry violation, here *de lege*, because the symmetry is violated in the underlying physical laws (and thus the molecular hamiltonian), and not just in the solutions resulting from these laws. Interestingly, the difference between de facto and de lege symmetry breaking is more pronounced in quantum mechanics than in classical mechanics. Indeed, in classical mechanics, we get stable left and right handed states with or without asymmetric potential, and the small asymmetry is statistically insignificant even at very low temperatures. However, in quantum mechanics the small symmetry violation leads to a stabilization of the chiral (λ,ρ) states in the limiting case of $\Delta E_{PV} >> \Delta E_{\pm}$. In that case the states χ_+ and χ_- become unstable, time dependent, with an interconversion time

$$t(+ \rightarrow -) = \frac{1}{2}\tau_{\pm} = \frac{1}{2}\frac{h}{\Delta E_{PV}} \tag{21}$$

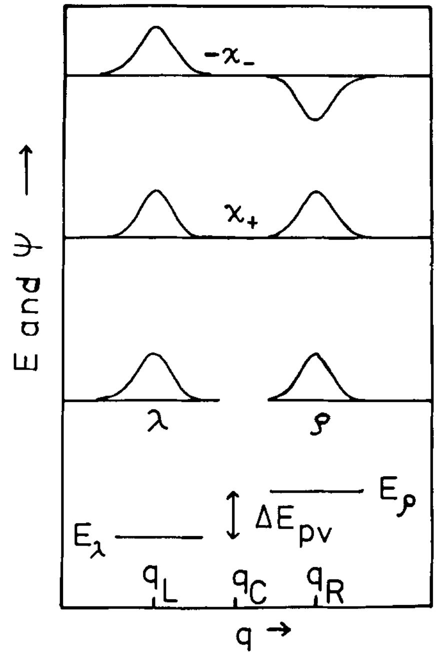

Figure 6. Quantum mechanical energy levels and wave functions for an asymmetric potential with parity violating energy difference ΔE_{PV} (see also fig. 5 and fig. 4).

The situation is illustrated in figure 6, which is to be compared with figure 5. The parity violating energy difference ΔE_{PV} leads to parity (quantum number +1 or −1) being not any more a constant of the motion, but becoming time dependent. Theoretically, one may estimate for t(+ → −) times between hours and days. Experimentally, the parity violating energy difference remains unknown, but we have proposed realistic experiments for its measurement [38,39,100]. These experiments, which are both laser chemical and spectroscopic, would be of fundamental importance, in our opinion, and efforts are being started towards their realization.

One notes that, because of the parity violating energy difference, the two enantiomers in fig. 3 (or any others) are not any more, strictly speaking, exact mirror images of each other (one is more stable than the other, also structural parameters will not have exact mirror image relations). This raises a question of terminology. Barron [101] suggests *not* to use the term "enantiomers" for an ordinary optically active molecule and its isomer with the opposite sign for optical rotation of linearly polarized light, because of the absence of exact mirror symmetry, but rather to call true enantiomers the molecule (fig. 3) and its *mirror image composed of antiparticles*, which he supposes to be strictly equivalent because of CP invariance of the hamiltonian. However, as we shall see in the next section, this invariance is not well established and rather seems to be violated and thus the new definition of "enantiomer" does not solve the problem. We suggest to retain the well established usage of the word enantiomers for two optical isomers composed of just ordinary matter, with the understanding that enatiomers are just a special kind of isomers without *exact* energetic and mirror image equivalence (but still approximately so). This point will become even clearer in the next subsection.

4.3. Particle—Antiparticle Symmetry (C) and CP violation

It will be difficult to prepare complex molecules from antimatter in the laboratory and thus the symmetry considered here may not seem relevant to molecular structure and dynamics. It provides, however, further insight into the asymmetry of time and space in molecular physics. Consider figure 7, which establishes relations between left handed (L) and right handed (R) optical isomers composed of ordinary matter, and of antimatter (L* and R*).

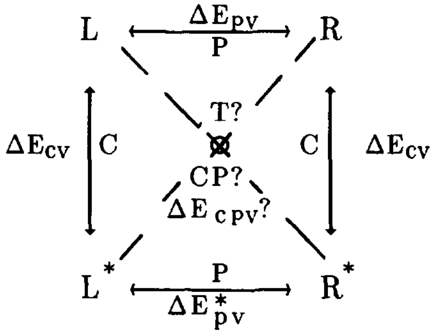

Figure 7 Scheme connecting various optical isomers composed of matter (L, R) and antimatter (L*, R*) with the symmetries P, C, CP (and T) and the energies connected with their violations (see also text), ΔE, index $_{pv}$ for parity violation, $_{cv}$ for C-violation and $_{cpv}$ for CP-violation.

As we have discussed, space inversion symmetry resulting in parity conservation (P) leads to the energetic equivalence of L and R and parity violation results in the hypothetical parity violating energy difference which is estimated to be of the order of 10^{-14} J mol^{-1} for some methane derivates. Although sign and magnitude of the effect remain uncertain, its *existence* can be considered to be well established through the parity violating β-decay [102]. The effect exists similarly for L* and R*. If we assume a deeper form of symmetry of space resulting in CP symmetry (simultaneous space inversion, P, and change from particles to antiparticles, then R* would be energetically equivalent to L and R to L* and thus violation of charge conjugation symmetry (C) would be as strong as parity violation

$$\Delta E_{pv} = \Delta E_{cv} \text{ with } \Delta E_{cpv} = 0 \tag{22}$$

The measurement of parity violating energy difference [38—40] would be equivalent to measuring the energy (and therefore rest mass) difference between L and its antimolecule L*. However, experiments on the K^0 meson decay provide unambiguous evidence for CP violation [93]. Although the effect is much weaker than parity violation, this introduces the possibility of CP violation in optically active molecules, hence

$$|\Delta E_{cv}| \simeq O(|\Delta E_{pv}|) \neq |\Delta E_{pv}|$$

$$\text{with } |\Delta E_{cpv}| << |\Delta E_{pv}| \tag{23}$$

The energy differences between L and L* and L and R are of the same order (O), but not any more identical. Indeed, all energies of the four "isomers" may now be different. This raises the interesting possibility of devising a significant new experiment, measuring the energy difference between L and R* associated with CP violation (if any). A direct spectroscopic experiment will be extremely difficult, because of the inaccessibility of antimolecules. However, because of the CPT theorem [103] CP violation implies T violation, which could be looked for directly in ordinary molecular processes and might be connected then to CP violating energy differences, provided one has some *quantitative* theory of the CPT connection, beyond the qualitative CPT theorem. This brings us back to our main topic: time dependent molecular dynamics.

4.4. Time reversal symmetry and irreversibility in intramolecular kinetics

Since Boltzmann's work the irreversibility of macroscopic phenomena has been understood as a *de facto* breaking of time reversal symmetry. The possibility of an underlying *de lege* symmetry violation is usually not mentioned, although it is suggested by the experiments on CP violation. We have the interesting situation that, while it is clearly *not necessary* to invoke a de lege T—asymmetry to explain irreversibility in the statistical mechanical molecular chaos, it still would be *possible* to do so. Experimentally the question could be resolved, for instance, by carrying out the momentum reversal shown in fig. 2 and observing that after 4 ps (or "returning to 0 ps"), one has no return to zero entropy but to some fluctuating finite value. In practice, following the scheme of fig. 1, one might also look for signatures of the effect in high resolution molecular spectra. We shall now briefly address this fundamental problem. The discussion parallels closely the discussion in section 4.1. and 4.2.

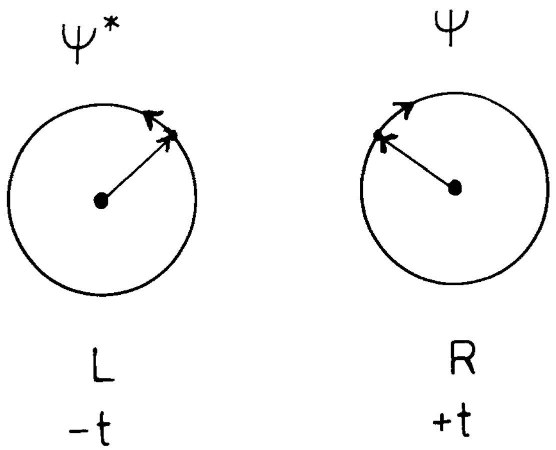

Figure 8 Two possible, symmetrically equivalent trajectories of a planet with different initial conditions for illustration of time reversal symmetry. If one interprets the radius vector as unit vector in the complex plane, one obtains an abstract representation of the "trajectory" of a quantum mechanical pendulum (the complex conjugate wave function Ψ^* corresponds to time reversal in Ψ).

Figure 8 illustrates time reversal symmetry and its de facto violation in the reversible classical mechanics of a planet's motion around the sun. If we have defined the absolute configuration of our coordinate system in space, using, for instance, the results on chiral molecules in the previous section, we can observe from top for a given initial condition a clockwise ("right-handed") motion with advancing time (+t) ("R" in fig. 8). If we run a movie of this motion backwards (—t), we observe the mirror image counter-clockwise ("left-handed"-L) motion. This would also be a possible motion for positive time, if we reversed at some time $t = 0$ the momentum vector of the planet. With a historically known initial condition this would seem unnatural to an inhabitant of the planet (a summer would follow after an autumn, if momentum reversal occurs in autumn), but is is mechanically perfectly possible with a different symmetrically equivalent initial condition. In classical mechanics, the planet can carry out only one of the two motions, the symmetry is always broken *de facto*. We can use the period of the planetary motion to define an absolute *time scale* (the old definition of the second was based on a fraction of the tropical year 1900), but not to define an absolute *direction of time*.

In the reversible quantum mechanics of isolated atoms and molecules (special case of Eqs. (3)—(11) with $\mathbf{H} = \mathbf{H}_{\mathrm{mol}} \neq f(t)$), one can expand the wavefunction with arbitrary, time independent coefficients c_k

$$\Psi(t) = \sum_k c_k \, \phi_k(r) \exp(-2\pi i E_k t/h) \qquad (24)$$

For the simplest example an equally weighted superposition of two states ϕ_1 and ϕ_2, which we may take real for simplicity, and energy difference $E_2 - E_1 = \Delta E$ one has

$$\Psi(r,t) = \frac{1}{\sqrt{2}} \exp(-2\pi i E_1 t/h)$$

$$\{\phi_1(r) + \phi_2(r)\exp(-2\pi i \Delta E t/h)\} \qquad (25)$$

The observable "trajectory" for the quantum mechanical motion is given by $|\Psi|^2 = \Psi\Psi^*$, i.e. just the relative phase $\exp(-2\pi i \Delta E t/h)$. This relative phase describes the trajectory of the unit vector in the complex plane. With positive ΔE ($E_2 > E_1$) and for positive time one has clockwise motion, for negative time (looking at the movie running backwards) one has counter-clockwise motion. Time reversal (reversal of momenta and spins) corresponds here to the transition from Ψ to Ψ^*, which also provides a possible solution of the time dependent Schrödinger equation for hermitean Hamiltonians. For the two quantum trajectories considered the time reversal symmetry is broken *de facto* in perfect analogy to the classical planetary motion. Incidentally, the modern SI definition of the time unit second makes use of Eq. (25) with two hyperfine levels of the ^{133}Cs-atom separated by 0.3066332 cm^{-1} or $\Delta E = 3.66815$ J mol^{-1} giving, more precisely, and by definition exactly 9192631770 periods for one second.

The new aspect in quantum mechanics is the possibility of a third solution by the superposition principle

$$\chi = \frac{1}{\sqrt{2}} (\Psi + \Psi^*) \qquad (26)$$

The atomic motion thus in a sense allows the "quantum planet" to exist in a symmetrical state which at the same time carries out clockwise and counter-clockwise rotation and where the symmetry is not broken de facto. The situation is the perfect analogue of the symmetrical, achiral states χ (+ and –) discussed for space inversion symmetry and we refer to section 4.2 for the corresponding discussion.

Returning now to the results presented in section 3 in the light of the present general discussion we find that the quasiclassical coupled molecular oscillator relaxation corresponds to the transition from a simple initial condition to a complicated trajectory with a time average of the probability density P corresponding to the microcanonical average in classical chaotic (and ergodic) systems

$$< P(r,t) >_t \cong P_{\text{microcanonical}}(r) \qquad (27)$$

The new aspect compared to the reversible planetary motion is that in the de facto symmetry breaking in a classical chaotic system we have this ergodic property and in addition the very subtle impossibility of exactly reverting the momenta (for lack of sufficient precision, in practice and in principle). The even stronger de facto symmetry violation in quantum mechanical, strongly anharmonic coupled oscillators with loss of quasiclassical molecular structure implies

$$|\Psi(r,t)|^2 \simeq <|\Psi(r,t)|^2>_t \qquad (28a)$$

$$P(r,t) \simeq <P(r,t)>_t = P(r)_{\text{microcan.}} \qquad (28b)$$

The duality of quantum dynamics with two times for relaxation, one quasiclassical, τ(CIVR), one for delocalization τ(DIVR) finds an analogy in the racemisation kinetics of optical isomers λ and ρ [39]. There we would have classically just one racemisation time for equilibration of λ and ρ (or R and S). In quantum mechanics we can consider the case of large densities of states $\rho(E)$ with two limiting cases, firstly

$$\rho(E) >> \Delta E_{\pm}^{-1} >> \Delta E_{pv}^{-1} \qquad (29)$$

Then we have "nonclassical" relaxation of parity first with loss of parity and left–right structure formation. Secondly we have with

$$\rho(E) >> \Delta E_{pv}^{-1} >> \Delta E_{\pm}^{-1} \tag{30}$$

first classical structural relaxation (i.e. racemisation) and then nonclassical parity violation (one could invert the role of classical and nonclassical in the terminology). For details of these phenomena we refer to [39].

Obviously, the next step would be to search for a *de lege* violation of time reversal symmetry in molecular dynamics, which implies in terms of the matrix elements of the time evolution operator U from Eq. (4):

$$|U_{fi}|^2 \neq |U_{if}|^2 ? \tag{31}$$

that is a violation of the principle of **microscopic reversibility**

$$|U_{fi}|^2 = |U_{if}|^2 \tag{32}$$

This principle has often been tested and never found to be violated for isolated atomic and molecular systems. In contrast to parity violation we have no adequate theory to estimate the size of possible effects from the T-symmetry violation, which should exist, if we are allowed to transfer the results from CP violation to molecular physics by means of the CPT theorem. An experimental search would clearly be very difficult unless one hopes for sheer luck.

4.5. Summary of current status of symmetry violations in molecular quantum dynamics

Reconsidering the list of symmetries at the beginning of this chapter we may briefly summarize here the current status of symmetry violations in molecular quantum dynamics. Because of the fundamental significance of these questions there are connections to all branches of science, including, in particular, cosmology. As already mentioned, there is no serious experimental (or even solidly founded theoretical) evidence for a violation of any of the continuous symmetries of time and space leading to energy-, momentum-, and angular momentum conservation. However, energy conservation has been hypothesized to be violated on several occasions, most prominently in continuous matter creation in the steady state cosmology of Bondi, Hoyle and Gold. In a similar fashion one could invoke here momentum and angular momentum non-coservation on purely speculative grounds.

The symmetries of space and time inversion (P and T) result from the Schrödinger equation with a hamiltonian including the usual forces of atomic and molecular physics [104] and charge conjugation symmetry results from ordinary quantum electrodynamics [105]. One obviously must distinguish here between the symmetry resulting from a theory and the one observed in experiments. In actual fact one finds experimentally violation of parity conservation (P) and of charge conjugation symmetry (C), which can be included into a new theory of atomic and molecular phenomena, that takes the weak interaction into account and retains the combined CP symmetry. It is interesting to relate this to some cosmological and biological findings. Estimating from the universal black body background of 2.7 K and the "visible" galaxial masses the baryon:photon number ratio to be n(baryon):n(photon) = 10^{-9} with essential absence of antimatter in the current universe, one finds for the "high-temperature" primordial pre-annihilation ratio

$$\frac{n_{\text{particles}}}{n_{\text{antiparticles}}} \simeq \frac{10^9+1}{10^9} \tag{33}$$

i.e. a very small violation of the C-symmetrical 1:1 ratio. Of course, the post-annihilation ratio corresponds to the total preponderance of matter over antimatter, the symmetry being broken de facto and de lege. We can compare this to the situation in asymmetric biological D- and L-aminoacids. Here the estimated "high temperature (300 K)" equilibrium ratio corresponds roughly to n(L):n(D) $\simeq$ $(1+10^{-18})$:1 by a very small de lege violation of parity conservation (P). However, after biochemical evolution and selection we find nowadays (almost) complete preponderance of the L-aminoacids in proteins, which might be de facto or de lege. We can consider this as a fossil of primordial evolution, as we would consider the existence of matter to be a fossil from the early big bang (leaving no anti-matter).

Beyond C and P violation we can now consider combined CP, which is a symmetry of some theories [106], which also would invoke T-symmetry. The violation of CP in the K^0-meson decay, which presumably implies T violation is one of the most striking experimental observations of current physics, still not well understood theoretically. Extending the above evolutionary considerations, we can by reference to fig. 7 state that the preponderance of L-amionacids in biological matter (over any of the other three L*, D, D*-aminoacids) may be a fossil telling a story about CP (and T). CP violation in the K^0-meson experiment is, by the way, the key to transmitting information about the *absolute* configuration of chiral molecules including resolution of any matter-antimatter ambiguity between far distant galaxies, which is a nice side-result for the astrobiochemist of the future [40]. Finally T-asymmetry de facto embedded in the present day macroscopic world may be considered to be perhaps a fossil from evolution out of the microscopically T-violating quantum event of the big bang.

Having entered now the realm of specuation, we might further speculate about possible violations of the last discrete symmetry in the list. If C, P, and T had to go, we might think that the Pauli principle will have to go as well [94,95]. A corresponding de lege violation of the symmetry in the hamiltonian could be expressed as the existence of non-Pauli q-isomers of elementary particles, which could be distinguished from the "regular" p-isomers. Since the discovery of the Pauli principle for electrons in 1925 from atomic spectra [107,108], this has been severely tested by atomic spectroscopy and never been found violated. We have considered Pauli-tests for heavy particles by looking at molecular spectra. Our repeated search for Pauli-forbidden lines in the high resolution Fourier transform infrared spectrum of CO_2 has resulted in a bound for the possible occurrence of non-Pauli ^{16}O (q-isomer) nuclei of nq:np $< 10^{-6}$ to 10^{-7} relative abundance compared to the "regular" Pauli (p-isomer) nuclei [94,100]. Circumstantial evidence for forbidden structure below this level is presumably unreal but suggests a more sustained effort [100]. Fox has proposed [95] to look for combined violations of parity conservation and Pauli principle in spectra of tetrahedral molecules such as RuO_4 [109]. If we consider ordinary methane with four non-Pauli (q-isomeric and thus distinguishable) protons, this would be chiral (figure 3). A cosmological view of the current, apparently Pauli obeying universe is to consider it to be "too young" to show the asymmetry prominently. Whereas expansion, annihilation and biological evolution have already resulted in maximal apparent violations of C and P (at least de facto), we would still have to wait for non-Pauli distinguishable particles to evolve, unless one considers macroscopic distinguishability of objects to reflect non-Pauli behaviour. This would be at least an attractive speculation similar to the other apparent macroscopic asymmetries of time, chirality and leptonic and baryonic matter, which concludes the speculations about the discrete symmetries.

5. CONCLUDING REMARKS

We have shown, how by the systematic approach summarized in the scheme of figure 1 deep insights can be gained into both molecular structure and molecular motion from high resolution molecular spectroscopy. While molecular spectroscopy is a mature research area with many useful down-to-earth analytical applications of molecular composition and structure of matter, as can certainly be appreciated by looking at many articles from this conference [110], we can use it also to address some of the most fundamental questions of current scientific research. Some aspects of molecular quantum dynamics belong to these, connecting the fields of spectroscopy and the complementary time dependent molecular kinetics [9,10,17–20].

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