From Molecules in Motion to Quantum Chemical Kinetics, Laser Chemistry and Molecular Parity Violation

With compliments from
Prof. Martin Quack
ETH Zürich
Laboratory for Physical Chemistry
ETH Hönggerberg HCI
Wolfgang-Pauli-Strasse 10
CH-8093 Zürich, Switzerland

Researchers: Sieghard Albert, Michael Gottselig, Michael Hippler, Hans Hollenstein, Roberto Marquardt, Lars Oeltjen, Martin Quack, Heiko Schmid, Georg Seyfang, Achim Sieben, Jürgen Stohner, Martin Willeke

Institute/   Group for Molecular Kinetics and Spectroscopy (Martin Quack)
Group   Laboratory for Physical Chemistry, ETH Zürich
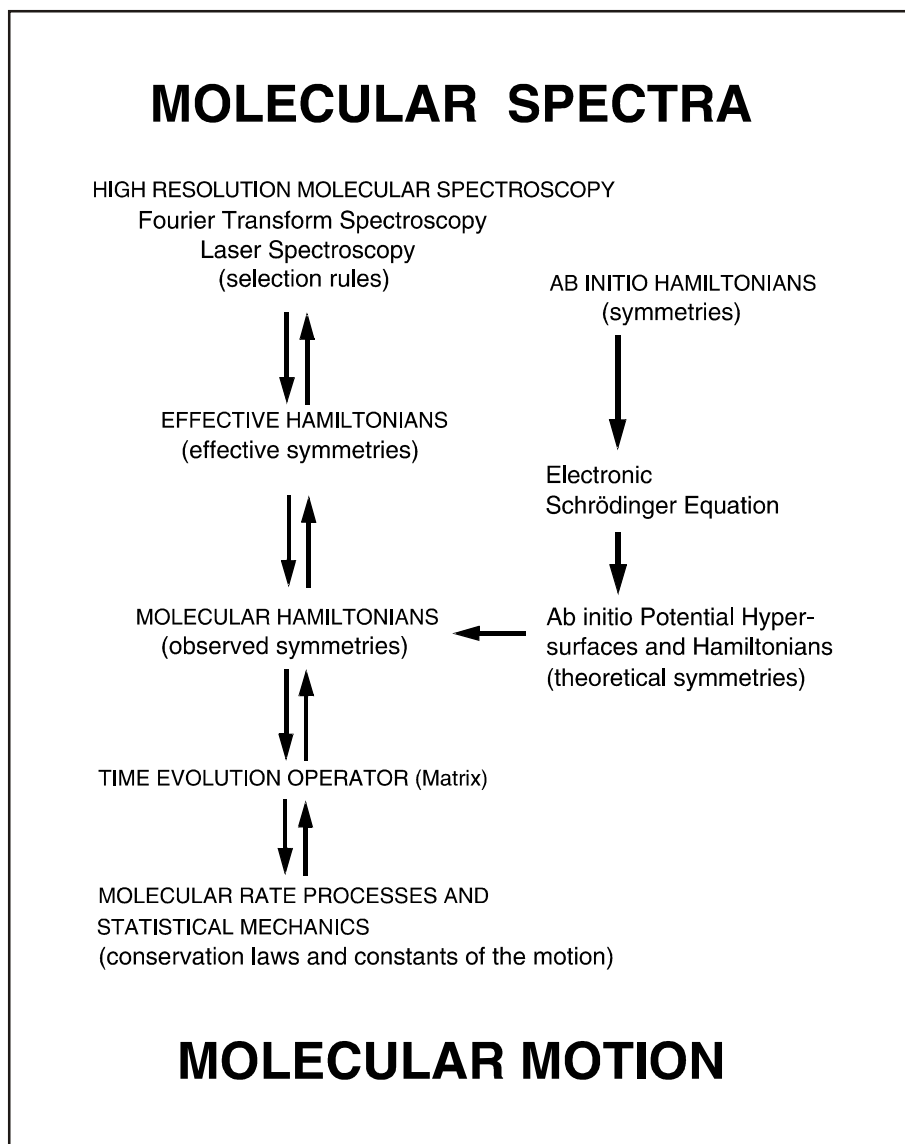
Abstract

The group for molecular kinetics and spectroscopy at ETH Zürich investigates the fundamental physical-chemical primary processes of chemical reactions. We have developed a conceptually new approach to derive these primary processes of intramolecular kinetics on time scales leading into the femtosecond and subfemtosecond (attosecond) domain on the basis of infrared spectroscopy with high frequency resolution but without short-time resolution. Selected applications include intramolecular quantum wavepacket dynamics of chemical functional groups of isolated, individual molecules and IR-laser chemistry of molecules under infrared multiphoton excitation, hydrogen bond tunneling dynamics in hydrogen fluoride clusters $(HF)_2$ and the tunneling stereomutation of prototypical chiral molecules. One of the greatest current challenges is the elucidation of the influence of the parity violating weak interaction mediated by the Z-Boson of high energy physics on the dynamics of chiral molecules. While the Z-Boson has a lifetime of less than a yoctosecond (10^{-24} s), the time scales for molecular parity violation are calculated to fall in the range of seconds. These processes of molecular parity violation can be compared to the processes of tunneling stereomutation in chiral molecules which extend from the femtosecond time scale to times that exceed the age of the universe by many orders of magnitude.

1. Introduction: Molecular Kinetics and Spectroscopy from the Schrödinger equation and quantum chemical kinetics

We have developed a conceptually new approach to investigate fast intramolecular primary processes with effective time resolutions reaching about 0.2 fs (200 as = 2 x 10^{-16} s) in practice, and even better, in principle [1-12]. This approach starts out from high frequency resolution spectroscopy of polyatomic molecules (but no, or unimportant time resolution) to derive the true molecular quantum motion at short time, either in isolation [12] or with strong laser irradiation, which may control molecular motion [13]. The method of analysis is the time dependent (and time independent) Schrödinger equation (in modern notation – very similar to the original one [14]), Eq. (1), solved by Eq. (2). Obviously, the approach makes use of substantial computation in several steps of the analysis.

$$i \frac{h}{2\pi} \frac{\partial \Psi(q,t)}{\partial t} = \hat{H}\, \Psi(q,t) \tag{1}$$

$$\Psi(q,t) = \hat{U}(t,t_0)\Psi(q,t_0) \tag{2}$$

MOLECULAR SPECTRA

HIGH RESOLUTION MOLECULAR SPECTROSCOPY
Fourier Transform Spectroscopy
Laser Spectroscopy
(selection rules)

AB INITIO HAMILTONIANS
(symmetries)

EFFECTIVE HAMILTONIANS
(effective symmetries)

Electronic
Schrödinger Equation

MOLECULAR HAMILTONIANS
(observed symmetries)

Ab initio Potential Hyper-
surfaces and Hamiltonians
(theoretical symmetries)

TIME EVOLUTION OPERATOR (Matrix)

MOLECULAR RATE PROCESSES AND
STATISTICAL MECHANICS
(conservation laws and constants of the motion)

MOLECULAR MOTION

Fig. 1: Scheme to derive fundamental processes of molecular kinetics from high resolution spectroscopy (after [12]).

The general, somewhat abstract scheme is outlined in Fig. 1. Molecular infrared spectra consist of many thousands of lines whose positions and intensities can be accurately measured. Their analysis provides in several complicated steps the molecular hamiltonian operator ($\hat{H}$ in Eq. (1), from which the time evolution operator ($\hat{U}$ in Eq. (2)) and the time dependent wavefunction $\Psi(q, t)$ are derived. $\Psi(q, t)$ contains all the relevant information on the time dependent molecular motion in the complete coordinate space (q). The experimental results can be compared with theoretical results derived from ab initio hamiltonians, which may also aid the analysis of experiments. For a detailed outline of this approach we refer to [9-13, 15-17]. We shall present here some exemplary applications.

2. Molecular Multiphoton Excitation and Infrared Laser Chemistry

These are new areas of chemical kinetics, where the analysis can either follow the traditional rate equation approach or the quantum chemical kinetics – Schrödinger equation (1) approaches. Indeed, it can be shown on the basis of the fundamental Schrödinger equation, under which conditions and in which form the rate equation approach may apply [13, 18]. The method consists in exciting molecular vibrations with many (typically between 10 and 50, but up to 500 or more) infrared photons. Typical times are between 1 ns and 500 ns. Recent applications concern the reactions of organic iodides such as

$$^{12,13}CF_3I \xrightarrow{nh\nu} {}^{12,13}CF_3 + I\,(^2P_{3/2}, F = 1,2,3,4) \qquad (n \cong 20) \qquad (3)$$
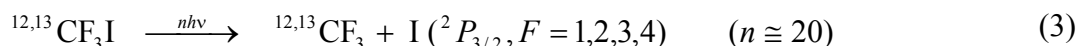
where for the first time the distribution of products over different hyperfine levels (F = 1, 2, 3, 4) could be measured and was found to be statistical, as is the product translational and internal energy on ns to ps time scales [19]. Computer simulations are used to analyze these results.

Another example is C_{60}, which after multiphoton excitation with about 500 infrared photons shows vibrational preionization, demonstrated for the first time for a neutral molecule in our work on this example [20]

$$C_{60} \xrightarrow{nh\nu} C_{60}^+ + e^- \qquad n \approx 500 \qquad (4)$$

and subsequent fragmentation

$$C_{60}^+ \xrightarrow{nh\nu} C_{58}^+ + C_2 \rightarrow C_{56}^+ + 2C_2 \qquad etc. \qquad (5)$$

This reaction sequence could be analyzed quantitatively by extensive master equation simulations following "case B" kinetics (see [4, 13].

Another interesting reaction was investigated in order to establish the transition between "case B" master equation kinetics and "case C" master equation kinetics [4, 13] as a function of molecular preexcitation [45]:

$$CH_3OH \xrightarrow{h\nu} CH_3OH^* \xrightarrow{nh\nu'} CH_3 + OH \qquad (6)$$

In this reaction sequence, in a first step an infrared laser is used to preexcite the methanol molecule with one or several quanta of the OH stretching vibration (fundamental or overtone transition with $h\nu$). Subsequently the thus preexcited methanol CH_3OH^* is further excited with n photons of a CO_2 laser to finally be dissociated into CH_3 + OH. Depending on the degree of preexcitation, nonlinear case C effects are more or less pronounced in the second step of multiphoton excitation. The nonlinear effects on this laser chemical reaction could be simulated quantitatively by the case C – case B master equation approach [4, 13, 45].

The most interesting fundamental questions in this kind of kinetics concern the role of intermolecular selectivity and of intramolecular selectivity as outlined in Fig. 2.

Intermolecular selectivity of the highly monochromatic laser excitation implies that we are able to select in a reaction mixture the molecules we desire for a chemical reaction. In particular, one can select different isotopomers of the same molecule (such as ^{12}C or ^{13}C in Eq. (4) and the method can be used rather routinely for efficient isotope separation following several schemes [21-23]. Today there is still hardly a useful market for the use of such isotopes, but once such a market evolves (for instance with potential medical applications of ^{13}C), the method can be made a starting point for an industrial process.

In contrast to intermolecular selectivity in a mixture of molecules, *intramolecular selectivity* would allow us to do some kind of selective molecular "laser surgery" within a single, isolated molecule (Fig.2). It turns out that the realization of this dream of "mode selective chemistry" requires a deeper knowledge of intramolecular processes.
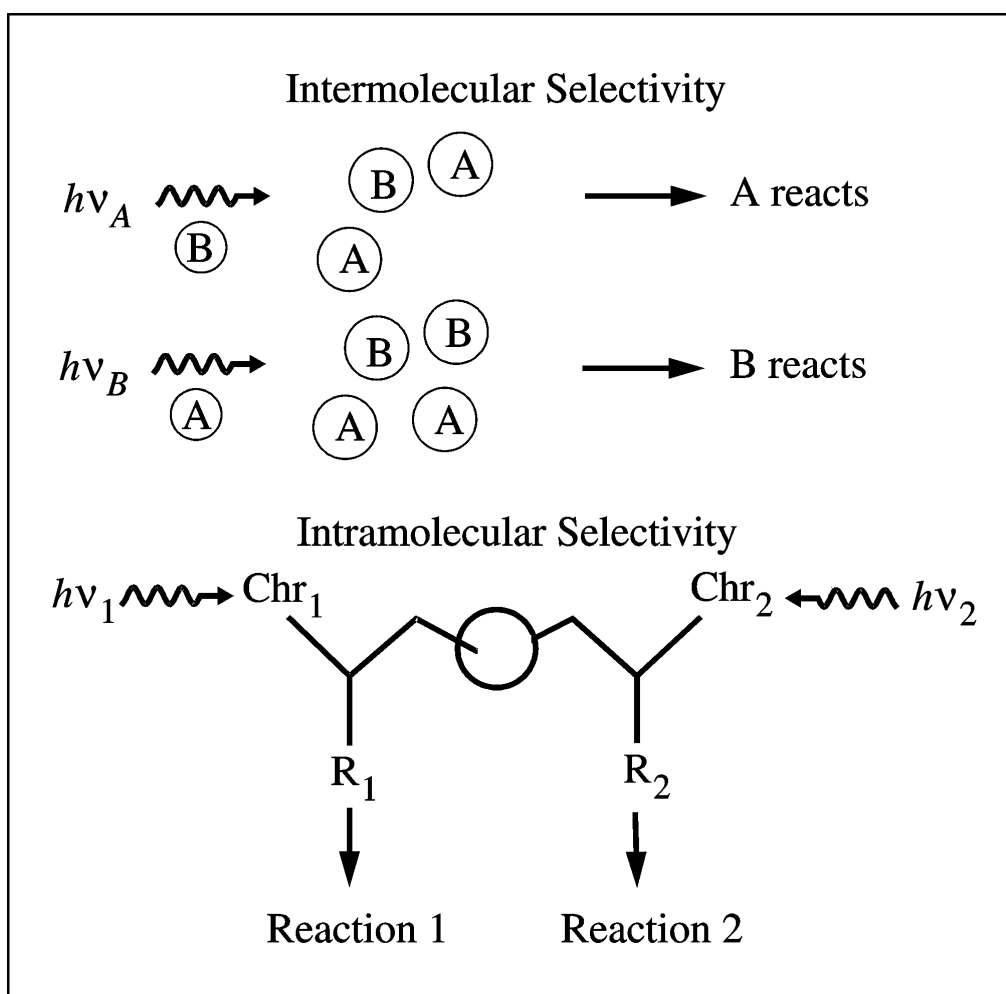
**Fig. 2:** Intermolecular and intramolecular selectivity in laser chemistry (after [21]).

3. Intramolecular vibrational redistribution and quantum wavepacket motion for the dynamics of functional groups

What happens in a molecule upon local excitation of an infrared chromophore (Fig.2)? How does the energy migrate from one part of the molecule to another? How do molecules *really* move? These questions are at the starting point of chemical reaction kinetics and shall be answered here for the fundamental example of just two coupled molecular vibrational modes in organic molecules o the type HCX_3, where for short times (up to 1 ps) just the C–H bond stretching and the C–H bending vibration exchange excitation energy. The quantum motion can be described by a two dimensional potential similar to a bathtub, with equipotential lines of the same potential energy being depicted in Fig. 3 [24]. One may consider the description of quantum motion like "waves in this bathtub", where the absolute square of the wave function ($|\Psi|^2$) gives the probability density of the position of the H-atom along a stretching or bending direction. There have been in the past two fundamentally different descriptions. In the first, the excitation remains localized in one or the other direction of motion (pictures N in Fig. 3, for "normal mode description"), depending on the initial excitation, perhaps with slow, periodic exchange between the two directions of motion.
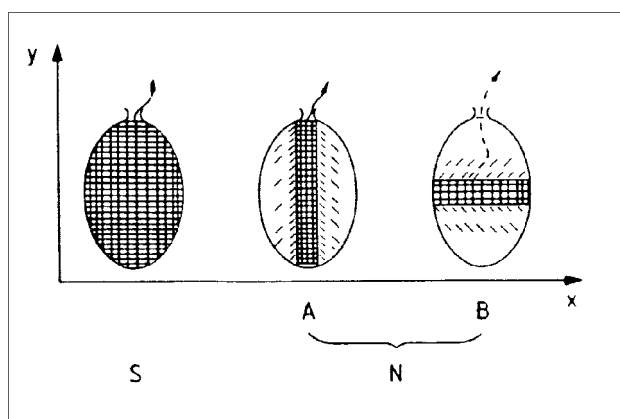
Fig. 3: Scheme of equipotential lines and probability distributions in a model of two coupled molecular vibrational modes.

In the other description, S in Fig. 3 (it forms the basis of statistical theories like the transition state theory of chemical kinetics), the excitation is delocalized on the average over the whole energetically accessible coordinate range. Fig. 4 shows how for the molecule CHF_3 an initial pure stretching excitation (0 fs) spreads over the whole coordinate range of stretching and bending in less than 100 fs. The probability densities $|\Psi|^2$ really look like waves covering the whole bathtub. The interpretation gives a loss of localized structure in addition to energy migration, a typical quantum mechanical effect [11, 25, 26]. While the result shown here dates back some time and is, indeed, the very first experimentally derived multidimensional molecular femtosecond wavepacket for energy migration, there have been numerous results since then, showing very different behaviour for this wavepacket evolution for different functional groups in molecules, for instance the R–C≡C–H group leads to rather long lived C–H stretching excitations with relatively slow energy migration (10 ps to 1 ns) and further interesting phenomena are observed for chiral XYZCH [27-29], aldehydic C–H in R–CHO [30, 58] and other characteristic chemical environments [15-17, 27, 28].
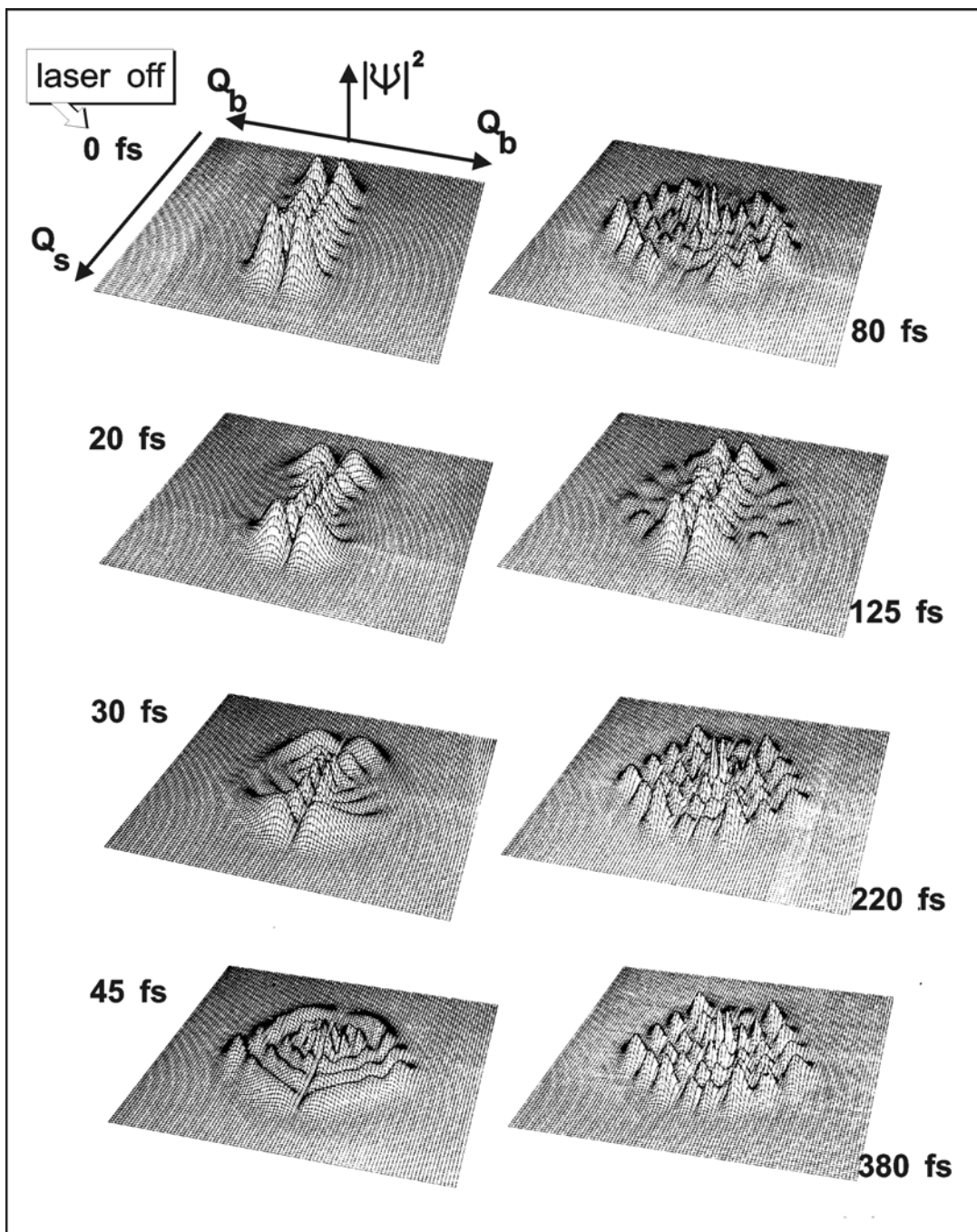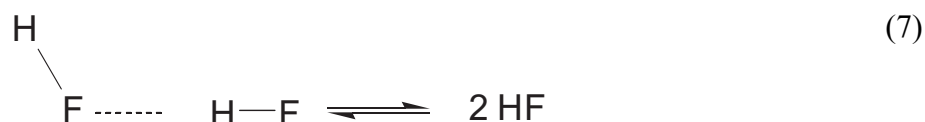
Fig. 4: Wavepacket motion for the two strongly coupled CH–stretching (Q_s) and CH–bending (Q_b) vibrations in the CHF_3 molecule $|\Psi(Q_s, Q_b, t)|^2$ is the probability distribution on the fs time scale after initial CH–stretching excitation at t = 0 (after [11])
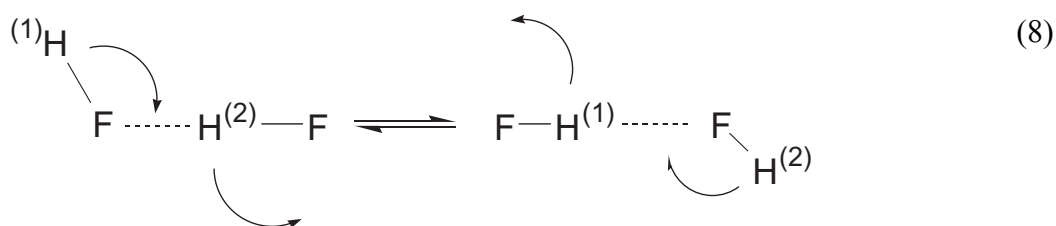
The discovery of mode selective energy migration [25-28] has opened numerous avenues for future studies. It is expected to replace old dogmas related to the transition state theory of chemical reactions and may allow the design of intramolecular energy transport in the future. For a recent general review of this subject we refer to [11]. Important recent developments concern the understanding of the C–H stretching and –O–H stretching mode couplings in highly excited methanol isotopomers such as CHD_2–OH [46] as well as the –OH and –C–H stretching coupling in formic acid [47]. Formic acid is an interesting case for several reasons. Firstly, we have shown in earlier work that formic acid in addition to existing as monomer can form two types of hydrogen bonded dimer, one (well established) closed form with two hydrogen bonds, one (newly observed) open form, with one hydrogen bond [8, 48]. Vibrational energy migration in these dimers can be studied by infrared and visible overtone spectroscopy and allows one to see effects from tuning Fermi-Resonances by tuning the OH stretching frequencies through hydrogen bonding, although it turns out that detailed analysis of these spectra is difficult [49] and presumably requires guidance through ab initio-calculations.

4. Tunneling reaction dynamics in hydrogen bonds of $(HF)_n$ complexes and in the stereomutation of simple chiral molecules

The quantum mechanical tunnel effect plays an important role in many areas of atomic and molecular physics and is expected to be particularly prominent in chemistry, whenever hydrogen atoms are involved in a reaction. It was discovered just 75 years ago at the dawn of modern quantum mechanics by Friedrich Hund [50]. As a first prototypical example studied by the spectroscopic approach described in Fig. 1 we mention hydrogen bond dissociation and rearrangement dynamics in hydrogen bonded $(HF)_2$:

$$\begin{array}{c} H \\ \backslash \\ F \text{------} \quad H \text{—} F \end{array} \rightleftharpoons 2\,HF \qquad (7)$$

and

$$\begin{array}{c} ^{(1)}H \\ \backslash \\ F \text{------} H^{(2)} \text{—} F \end{array} \rightleftharpoons F \text{—} H^{(1)} \text{------} \begin{array}{c} F \\ \backslash \\ H^{(2)} \end{array} \qquad (8)$$

These processes are of fundamental importance for our understanding of the dynamics of hydrogen bonded liquids such as hydrogen fluoride itself [31], but also water, which is similar, though more complex [51], and hydrogen bonds in biomolecules. We have been able to show that the switching process (8) depends strongly on the type of excitation of various vibrational and rotational modes in the complex, and falls in the range of 10–100 ps times. In contrast, the dissociation (i.e. evaporation like) can take much longer, even nanoseconds, even if the total energy in the complex is more than sevenfold the energy needed to break the

hydrogen bond (about 12.7 kJ mol^{-1}) [32]. Again, the *time* needed depends very strongly upon the *nature* of the initial excitation, not just the total amount of energy in the complex: It is highly mode selective, nonstatistical [31-34].

For more details and general reviews of this important topic of hydrogen bond dynamics in (HF)$_n$ clusters we refer to [30-33, 52, 53]. 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) 2 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 [33], a satisfactory experimental and theoretical solution has come about only very recently [34, 54]. Table 1 summarizes these results.

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 1: 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 [34, 54]). Theory is from the SO-3 surface [32].

The famous case of tunneling in ammonia stereomutation dynamics 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 [55] 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.

Another interesting and fundamental class of chemical reactions where we have observed this nonstatistical, highly mode selective behaviour, is the tunneling stereomutation in simple chiral prototype molecules such as nonplanar X–Y–Y–X molecules which are axially chiral [35] (such as hydrogen peroxide H–O–O–H or pyramidal amines (R$_1$R$_2$R$_3$N) [36, 37]. The

chemical reaction of stereomutation transforms the chiral R-enantiomer into the S-enantiomer (or P into M in axially chiral molecules):

$$R \rightleftarrows S \tag{9}$$
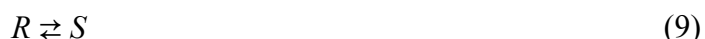
The time scales in aniline (–NHD) (C_6H_5–NHD) are 700 fs to a few ps, depending on whether promoting (catalyzing) or inhibiting modes are excited [36, 37]. Tunneling stereomutation in hydrogen peroxide is similarly mode selective with various excitations [35]. While such results are important for our current and future understanding of chemical reaction dynamics, the study of chiral molecules opens an avenue of research, that may prove revolutionary in the future of the fields bordering chemistry and physics and will be addressed in the last section of this short report.

5. The influence of Z-boson of elementary particle physics on the chemical dynamics of chiral molecules
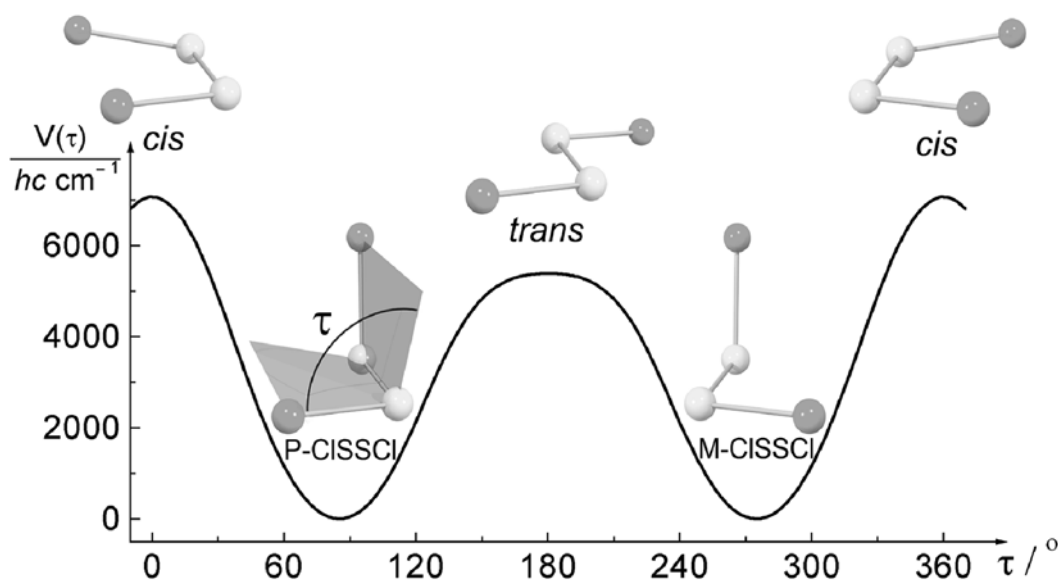
Fig. 5: Stereomutation in the chiral Cl–S–S–Cl molecule. The picture shows the symmetrical torsional potential for transforming the P-enantiomer into the M-enantiomer. There is an additional asymmetrical potential from the weak interaction, which is about 15 orders of magnitude smaller but governs the dynamics of chirality (after [44])

Figure 5 illustrates the stereomutation of an axially chiral molecule Cl–S–S–Cl in a simplified one-dimensional potential diagram. In the traditional quantum chemical picture, such a potential arises in the framework of the Born Oppenheimer approximation using as foundation the electromagnetic interaction, as one of the four fundamental interactions of physics, which leads to an exact symmetry and energetic equivalence of the enantiomers. This symmetry is in fact independent of the particular approximation and depends only upon the fundamental physical interactions incorporated in the treatment. These fundamental interactions are distinguished "ab initio" by their symmetries (see Fig. 1), which can thus be

tested. Whereas the electromagnetic interaction is mediated by photons and shows the inversion symmetry mentioned, which leads to conservation of the quantum number parity, the Z-boson mediates the so-called weak interaction, which adds an effectively antisymmetric potential to the one shown in Fig. 5. Thus the two enantiomers are no more energetically equivalent, but have slightly different energies. It turns out that these energy differences are exceedingly small, on the order or 10^{-11} Jmol^{-1}. Only recently have accurate calculations of this effect been possible [38-40], showing that it is in fact orders of magnitude larger than previously anticipated. Experiments to measure the energy difference have been proposed, but have not yet been carried out [41, 42]. Whether or not the energy differences are important, depends upon the relative magnitudes of tunneling splittings $\Delta E_\pm$ for stereomutation in the symmetrical case and of parity violating energy asymmetries ΔE_{pv}. Most recent calculations have for the first time shown the transition between several regimes of chiral molecules, those like H_2O_2 and aniline–NHD, where parity violation is in fact unimportant, and those like S_2Cl_2, where parity violation dominates. Indeed, the time for parity change is estimated here to be about 15 s only, whereas the tunneling stereomutation time in the hypothetical symmetrical, parity conserving case would exceed the age of the universe. D_2S_2 and T_2S_2 fall in an interesting intermediate range [43, 44]. These results change our understanding of the dynamics and kinetics of chiral molecules (Table 2).

Molecule [Ref.]	$\dfrac{\Delta E_{pv}}{(hc)\,\mathrm{cm}^{-1}}$	$\dfrac{\Delta t_{pv}}{\mathrm{s}}$	$\dfrac{\Delta E_\pm}{hc\,\mathrm{cm}^{-1}}$	$\dfrac{\tau}{s}$
H_2O_2 [35, 38, 40]	4×10^{-14}	400	11	3×10^{-12}
D_2O_2 [35, 40]	4×10^{-14}	400	2	2×10^{-11}
HSOH [56]	4×10^{-13}	40	2×10^{-3}	16×10^{-9}
DSOD [56]	4×10^{-13}	40	1×10^{-5}	3×10^{-6}
TSOT [56]	4×10^{-13}	40	3×10^{-7}	0.1×10^{-3}
H_2S_2 [39, 43]	1×10^{-12}	16	2×10^{-6}	2×10^{-5}
D_2S_2 [43]	1×10^{-12}	16	5×10^{-10}	0.07
T_2S_2 [43]	1×10^{-12}	16	1×10^{-12}	33
S_2Cl_2 [44]	1×10^{-12}	16	$\ll 10^{-70}$	$\gg 10^{60}$

Table 2: Parity violating ΔE_{pv} energy differences 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 only for survey).

In the more distant future, this kind of spectroscopic investigation on chiral molecules might lead to fundamentally new physics in relation to the symmetries C, P, and T, to our

understanding of the symmetry of space and time directions, and the possibility of an absolute molecular clock defining a time direction, not just time intervals [42]. This interesting field of investigation in our project has been recently reviewed also in relation to the evolution of biomolecular homochirality [57].

Acknowledgement

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