Molecules in Motion

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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 domain on the basis of infrared spectroscopy with high frequency resolution but without short-time resolution. Selected applications include intramolecular 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.

Keywords: High-resolution infrared spectroscopy · Infrared multiphoton excitation · Molecular kinetics · Parity violation in chiral molecules · Quantum dynamics

1. Introduction: Molecular Kinetics and Spectroscopy from the Pseudo First Order Rate Law to the Schrödinger Equation and Quantum Chemical Kinetics

The history of chemical kinetics is deeply linked to time-dependent spectroscopic observation. Indeed, the starting point of quantitative chemical kinetics was the formulation of a time-dependent pseudo first-order rate law for the spectroscopically observed hydrolysis ('inversion') of cane sugar (Z for the concentration of 'Zucker') in 1850 by Wilhelmy [1], given in Eqn. (1) in its original form

$$-\frac{dZ}{dt} = M \cdot Z \cdot S \qquad (1)$$

where the concentration of the catalyst (acid, with S for concentration of 'Säure')

is considered as constant as well as the proportionality factor M, which today would be called the rate constant.

With the additional concept of reaction mechanisms composed of elementary reactions, much of today's chemical reaction kinetics studies follow these lines, with major progress having been made in terms of time resolution, reaching microseconds with the relaxation [2] and flash photolysis [3] techniques of the 1950's and a few femtoseconds today [3–5] (excepting for the famous 0 fs pulses [6]). Bimolecular reactions have also been investigated by the conceptually independent approaches of molecular beam scattering [7] (see also the general reviews [8–11]).

We have developed a conceptually new approach to investigate fast intramolecular primary processes with effective time resolutions reaching about 0.2 fs in practice, and even better, in principle [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 Eqn. 2 – very similar to the original one [14]), solved by Eqn. (3)

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

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

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 Eqn. (2), from which the time evolution operator ($\hat{U}$ in Eqn. (3)) 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 (1) ap-

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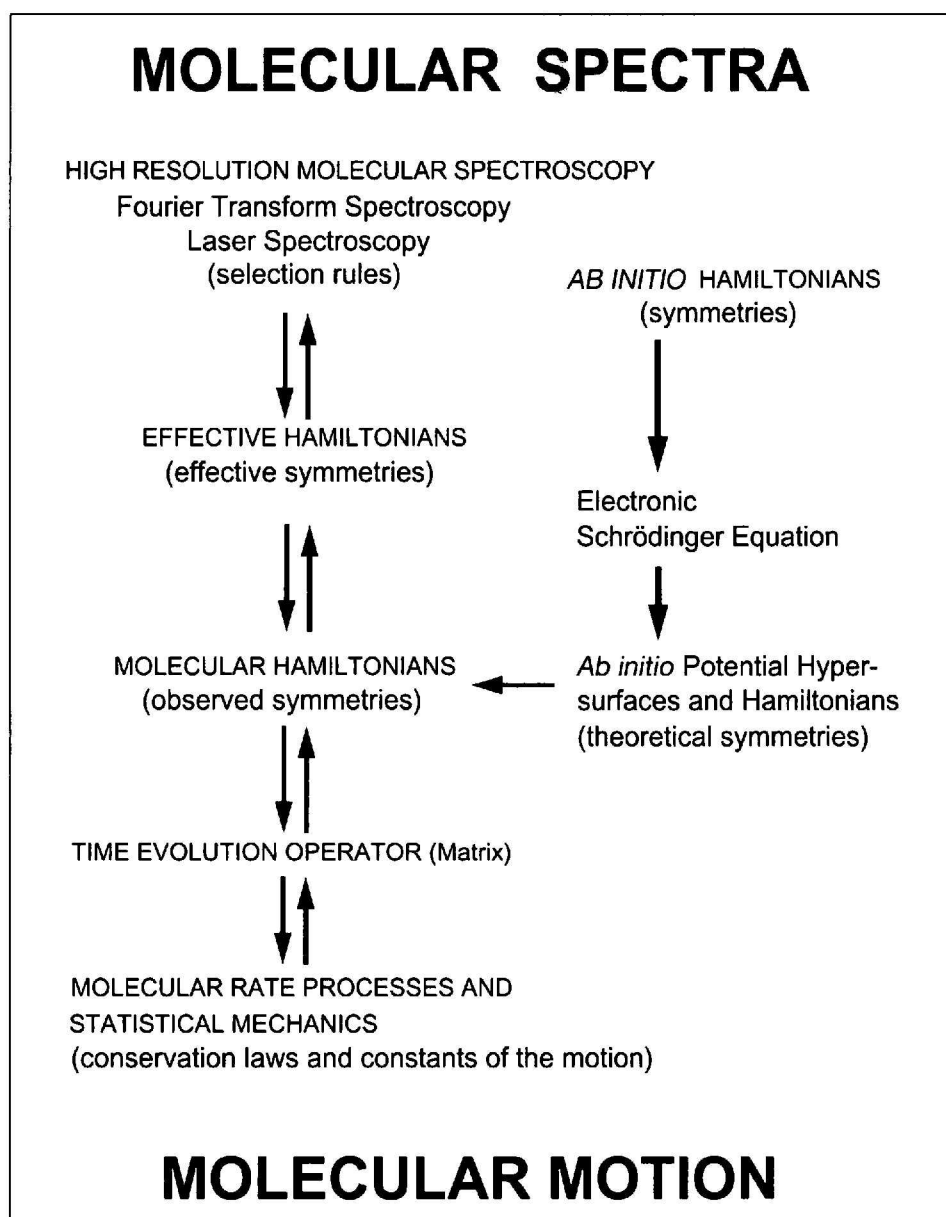E-Mail: Martin@Quack.CH
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MOLECULAR SPECTRA

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])

proach or the quantum chemical kinetics – Schrödinger equation (2) 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) infrared photons. Typical times are between 1 ns and 500 ns. Recent applications concern the reactions of organic iodides such as in Eqn. (4)

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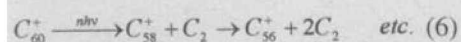
$$(n \cong 20) \tag{4}$$
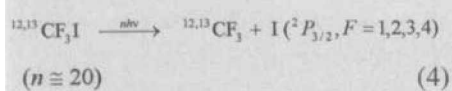
where for the first time the distribution of products over different hyperfine levels ($F = 1, 2, 3, 4$) could be measured and was found to be statistical, as is the product translational and internal energy on ns to ps time scales [19].

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

$$C_{60} \xrightarrow{nh\nu} C_{60}^+ + e^- \qquad n \approx 500 \tag{5}$$
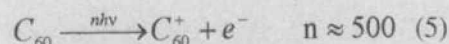
and subsequent fragmentation

$$C_{60}^+ \xrightarrow{nh\nu} C_{58}^+ + C_2 \rightarrow C_{56}^+ + 2C_2 \quad etc. \tag{6}$$

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 im-

plies 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 Eqn. (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.

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 of the type HCX_3, where for short times (up to 1 ps) just the C–H bond stretching and the
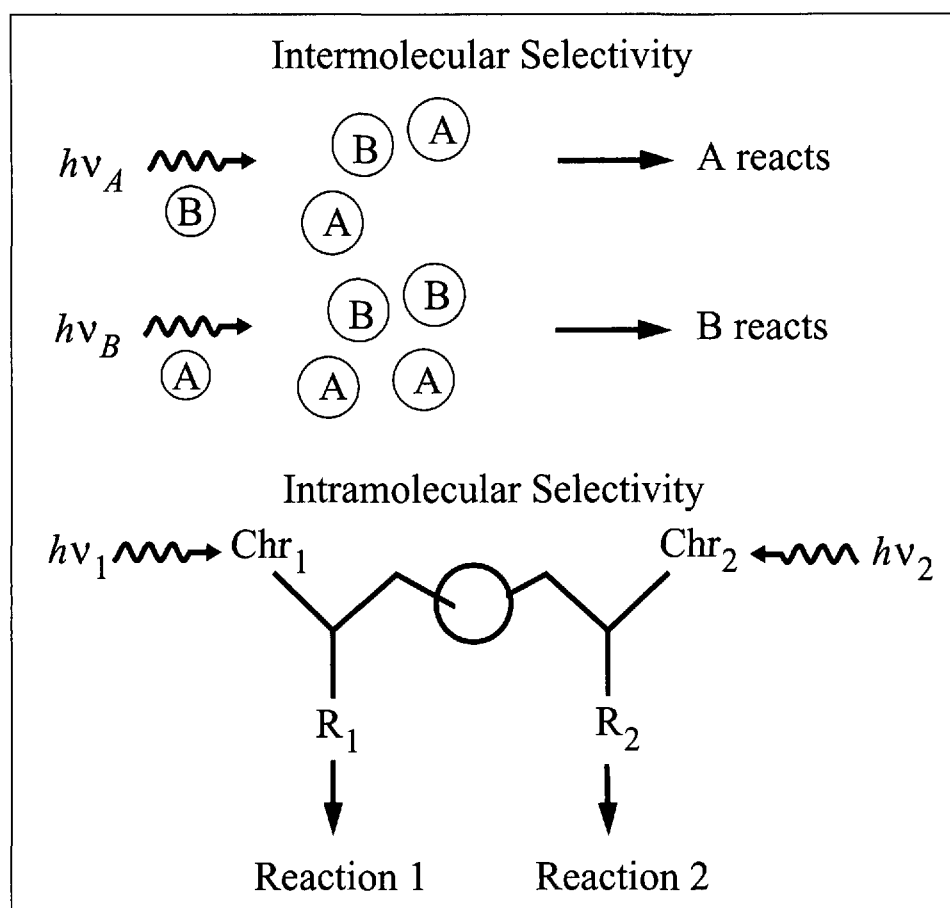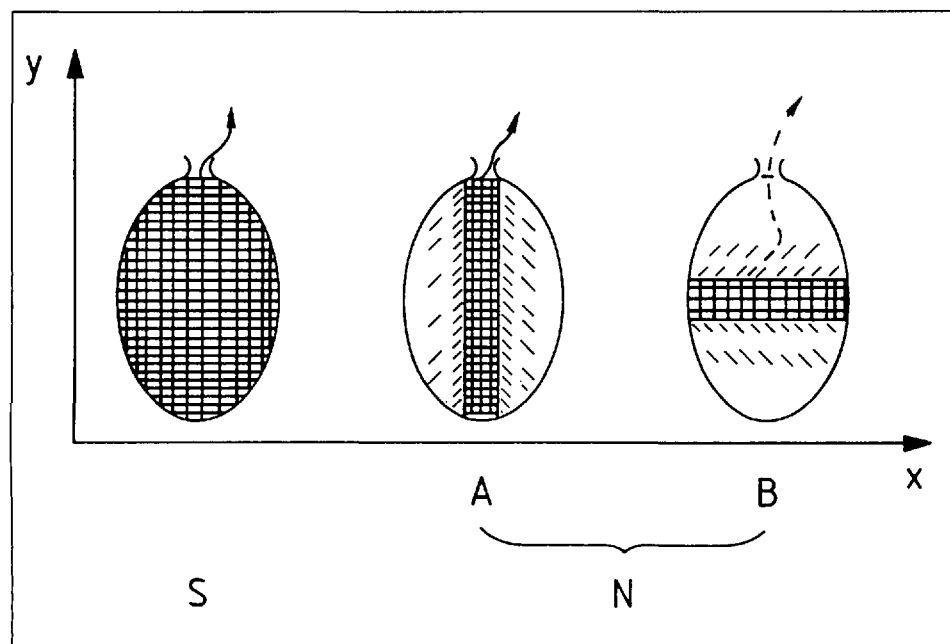
Fig. 2. Intermolecular and intramolecular selectivity in laser chemistry (after [21])

mode description'), depending on the initial excitation, perhaps with slow, periodic exchange between the two directions of motion.

In the other description, S in Fig. 3 (which 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 behavior 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] and other characteristic chemical environments [15–17][27][28]. 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.

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

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

Fig. 3. Scheme of equipotential lines and probability distributions in a model of two coupled molecular vibrational modes (after [24])
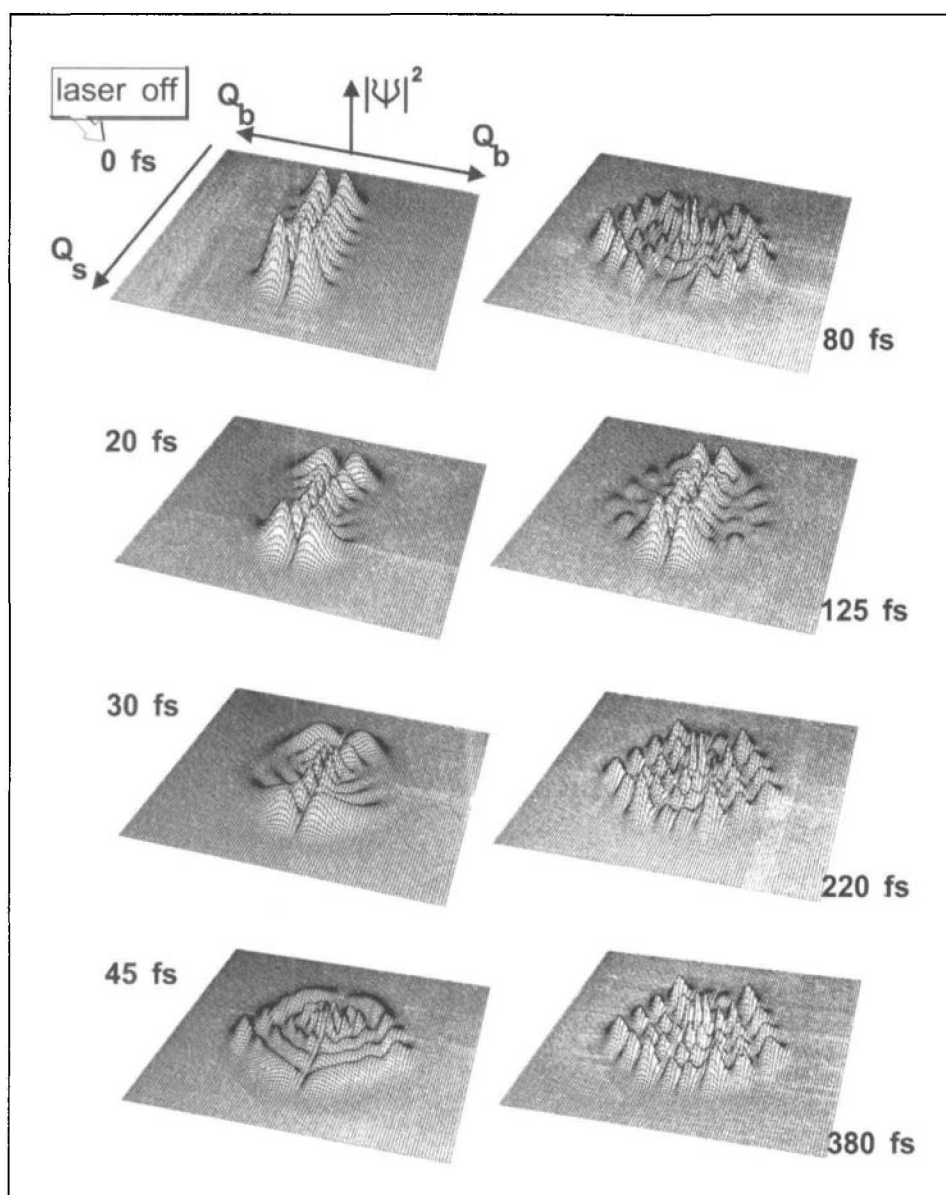
Fig. 4. Wavepacket motion for the two strongly coupled CH–stretching (Q_s) and CH–bending (Q_b) vibrations in the CHF_3 molecule $|\Psi(Q_s, Q_b, t)|^2$ is the probability distribution on the fs time scale after initial CH–stretching excitation at $t = 0$ (after [11]

chemistry whenever hydrogen atoms are involved in a reaction. As a first proto-typical example studied by the spectro-scopic approach described in Fig. 1, we mention hydrogen-bond dissociation and rearrangement dynamics in hydrogen bonded $(HF)_2$:
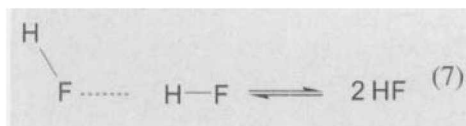
And
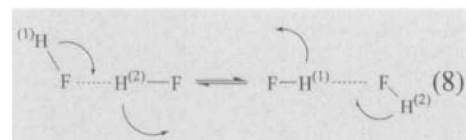
These processes are of fundamental importance for our understanding of the dynamics of hydrogen-bonded liquids such as hydrogen fluoride itself [31], but also water, which is similar, though more complex, and hydrogen bonds in biomol-

ecules. We have been able to show that the switching process (7) depends strongly on the type of excitation of various vibra-tional and rotational modes in the com-plex, 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 ener-gy 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 and nonstatistical [31–34].

Another interesting and fundamental class of chemical reactions where we have observed this nonstatistical, highly mode selective behavior, 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 $(R_1R_2R_3N)$ [36][37]. The chemical reaction of stereo-mutation transforms the chiral R-enanti-omer into the S-enantiomer (or P into M in axially chiral molecules):

$$R \rightleftarrows S \qquad (9)$$

The time scales in aniline (–NHD) $(C_6H_5$–NHD) are 700 fs to a few ps, de-pending on whether promoting (catalyz-ing) or inhibiting modes are excited [35][37]. Tunneling stereomutation in hydrogen peroxide is similarly mode se-lective 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 re-search that may prove revolutionary in the future of the fields bordering chemis-try and physics and will be addressed in the last section of this short report.

5. The Influence of the Z-Boson of Elementary Particle Physics on the Chemical Dynamics of Chiral Molecules

Fig. 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 a 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 of 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 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).

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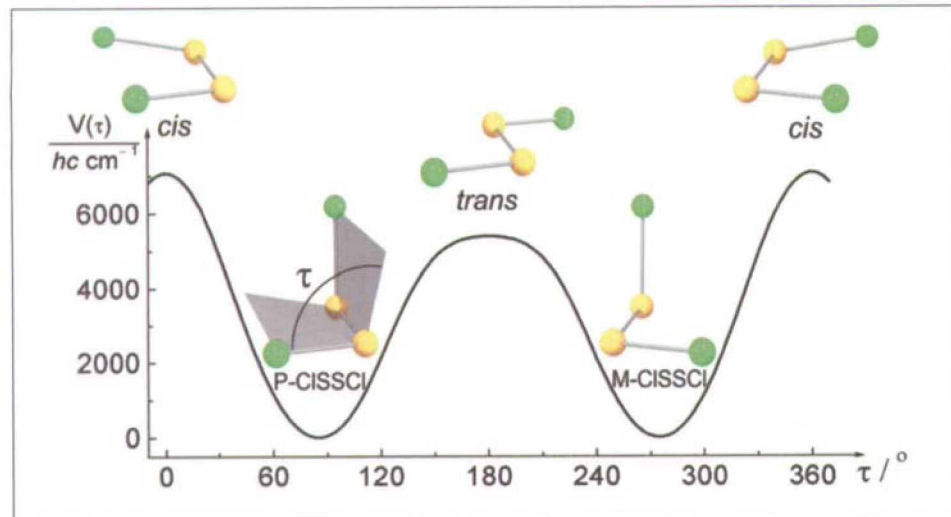
Fig. 5. Stereomutation in the chiral Cl–S–S–Cl molecule. The picture shows the symmetrical torsional potential for transforming the P-enantiomer into the M-enantiomer. There is an additional asymmetrical potential from the weak interaction, which is about 15 orders of magnitude smaller but governs the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

Molecule [ref.]	$\dfrac{\Delta E_{pv}}{(hc)\,cm^{-1}}$	$\dfrac{\Delta t_{pv}}{s}$	$\dfrac{\Delta E_{\pm}}{(hc)cm^{-1}}$	$\dfrac{\tau}{s}$
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}
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. 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.

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