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The ORCHID project: a search for the Origin of Chiral Discrimination**

Abstract – Control of translational, internal and orientational molecular degrees of freedom in elementary chemical processes constitutes a challenge for the modeling and applications of physical chemistry. In this paper, we focus on the peculiar part arguably played by orientational control for unveiling the stereodynamical nature of processes involving molecular chirality – one of the most fascinating issues of molecular science, crucial in view of the intriguing ubiquitous role of selective left-right asymmetry in the bio-world. Typically, investigations of processes involving explicitly molecular chirality exploit circular polarization, *e.g.* from laser and/or synchrotron radiation sources. We take an alternative stereodynamical view that relies on advances in molecular-beams orientation techniques: (i) through gas flowing in supersonic regimes, designated as «natural», not requiring external fields and (ii) using elec-

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** The research project ORCHID is an integrated search of stereodynamical mechanisms for the ORigin of CHIral Discrimination by oriented molecular beams, synchrotron radiation, molecular dynamics and computational modeling. It received financial support in 2015, by the «Ministero per l'Istruzione, l'Università e la Ricerca» through the program SIR (Scientific Independence for Young Researchers) and is nowadays part of the Astrochemical Observatory.

trostatic techniques. These perspective corroborates the following objectives: (a) extension and probing of the natural orientation technique to chiral molecules by elastic and/or inelastic collisions, that permits to design crossed molecular beam experiments to be implemented for the first-time demonstration of left-right spatial asymmetry in molecular encounters; ii) the novel experimental proposals exploiting hexapolar orientation are applied to experiments on the orientation control of molecular collisions in dynamics and photochemistry.

1. *Introduction*

The experimental techniques and the interpretative tools of modern physical chemistry are applied in this work to specific issues regarding the broad theme of the origin and manifestation of molecular chirality [1, 2]. This theme has exceeded the scope of chemical research and is central also to the physical and biological sciences [3, 4]. The origin of chiral specificity as a signature of life on our planet, and the high enantiomeric selectivity of processes involved in the most important biological molecules, rank among the most intriguing natural phenomena that is of great interest, not only for basic research but also for technology (chiral recognition and asymmetric synthesis in organic, industrial and pharmaceutical chemistry). The recent discovery of propylene oxide, one of the simplest organic chiral molecules, in the interstellar medium [5] (and previously the discovery of hydrogen peroxide, arguably the simplest chiral molecule [6]), has provided additional interest on the occurrence of this phenomenon also in astrochemical environments.

Several hypotheses have been formulated on the natural origins of chiral discrimination in the bio-world. Some of them are controversial and none was convincing enough to receive global consensus. A scenario attributes chiral bias just to chance and statistical fluctuations, followed by some amplification mechanisms: crystalline solids of chiral compounds formed from a melt normally solidify as a racemic conglomerate, and yield an enantiomeric excess if crystallization occurs under constant stirring. A hypothesis considers that asymmetric distributions of enantiomers originated from parity violation, due to weak nuclear forces, leads to an energy difference between enantiomers of chiral molecules, but the energy difference is extremely small and the transmission of this asymmetry to the molecular scale has eluded theoretical modeling and experimental verification (see [7] and references therein).

On the other hand, polarized fields can certainly act as a chiral environment and there is plenty of experimental evidence concerning the role of electric and magnetic fields [8]. Enantioselective photochemistry with circularly polarized light is well established and experimental observations of dichroic effects in photoionization can be obtained by very intense synchrotron radiation sources [9, 10]. The magnetochiral dichroism induced by magnetic fields and unpolarized light may be enantioselective in photochemical reactions, and recently has been observed in organic molecules [11].

A key experiment has recently demonstrated preferential population of the rotamers in haloalkanes induced by whirling flows [12]. Such rotational-translational motions (vortices) are chiral force fields and are present in a large variety of contexts, from planetary atmospheres to the interstellar space. Also, liquid vortices have been shown to induce chiral discrimination in mesophase achiral aggregates [13]. It was theoretically proved that in collisions between unpolarized projectiles and chiral molecules, the differential cross sections for enantiomers differ if these are oriented: if a chiral framework is provided, the enantiomers will scatter the projectiles in different directions [14]. The key role of orientation has been further confirmed by experiments of scattering of polarized electrons by thin films of oriented chiral molecules impinging on surfaces [15], and by the demonstration of stereodynamic effects in scattering from surfaces of molecules oriented according to the techniques mentioned above [16]. Ionization cross sections of chiral molecules by electron impact have also been theoretically investigated, demonstrating the dependence of these observables on the polarization of the incident electron beam [17]. No experimental evidence has been provided on the left-right asymmetry of outcomes of molecular encounters, for which crucial is the unique availability of molecular orientation techniques (see [18] and references therein).

The control of translational and internal molecular states is a main challenge in the realization of stereodynamics experiments. Additionally, control of the molecular orientation is a fundamental prerequisite in order that the phenomenon of chiral selectivity can be demonstrated even without circularly polarized light: this is the strongest point towards the goal of establishing a phenomenology for the origin of chirality as a steric property in the area of chemical kinetics. To this aim, orientational techniques exploit innovative approaches based on (a) properties of expansions of gas mixtures in supersonic flow regimes and hexapolar electrostatic fields. Control through gas flows, referred to as the «natural» alignment technique, has been revealed and characterized in the Perugia laboratory, but knowledge of possible chirality effects in streams is in its infancy and has to be further investigated as a basic scientific issue, a bonus being to prove or disprove any role in prebiotic issues [19-26]. All this is motivating this project (see the logo in Fig. 1) involving the study of left and right asymmetries in elastic and inelastic angular distributions in the collisions of oriented chiral molecules, verifying the anticipation of molecular dynamics simulations, to be performed to design, assist and interpret the demanding experiments and their results. Control through hexapolar electric fields had been widely used for linear and symmetric-top molecules and is being adapted for the first time to the orientation of chiral molecules [27-30]. This requires dealing with molecules of an unprecedented complexity and an elaborate theoretical approach for data analysis. Crossed molecular beam experiments are being performed for the first-time demonstration of left-right spatial asymmetry in molecular encounters: these experiments allow us to obtain information on reaction mechanisms, on the partitioning of product energy and on features of the potential energy surfaces.

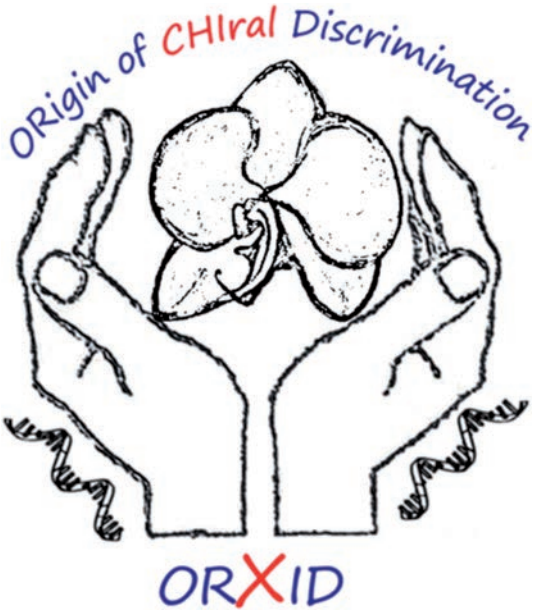


Fig. 1. The Orchid in the logo of the project not only stands for the acronym of ORigin of CHIral Discrimination, but is also appropriate being the great varieties of this flower often scrutinized for their chiral properties. One of them is the spiral arrangement of the five petals.

The paper is structured as follows: in Section 2, the theoretical models and computational simulations of chiral selective processes are reported; in Section 3, we describe the on-going molecular beam scattering experiments; in Section 4, we report the state-of-the-art of enantioselective photodissociation experiments; finally, in Section 5 we give concluding remarks.

2. *Theoretical models and computational simulations*

A preliminary assessment of enantioselective collisional mechanisms requires a detailed characterization of the potential energy surface that can describe accurately the intermolecular interactions. An efficient and accurate approach is based on semiempirical methods, which are tested and improved by comparison with results of electronic structure calculations and leads to suitable analytical expressions for the interactions, also by explicitly exploiting the strength and range parameters obtained from collision observables. This approach permits an internally consistent reproduction of the interactions of the most significant configurations of the systems, allowing us to perform extensive molecular dynamics simulations of collisions involving chiral molecules. Extensive investigations have been carried out on hydrogen peroxide and persulfide, which are arguably the simplest cases of chiral molecules

[31-33]. Molecular dynamics simulations of elastic collisions between oriented chiral molecules and rare gas atoms have shown that the latter are deflected with a specific angular distribution discriminating the two enantiomers [34]. For studies concerning unimolecular processes involving propylene oxide and its interactions with rare gas atoms see [35-37].

3. *Chirality discrimination in molecular collisions*

In this section, we describe two unique molecular-beams experiments of remarkable complexity, built and operating in the Perugia laboratory: chiral selection originates in molecular collisions and is determined by the different interaction between a couple of identical (RR) or different enantiomers (RS). Orientational control through the natural alignment technique would permit to highlight such a difference [37-39]. In Fig. 2, we report the configuration of an experimental apparatus

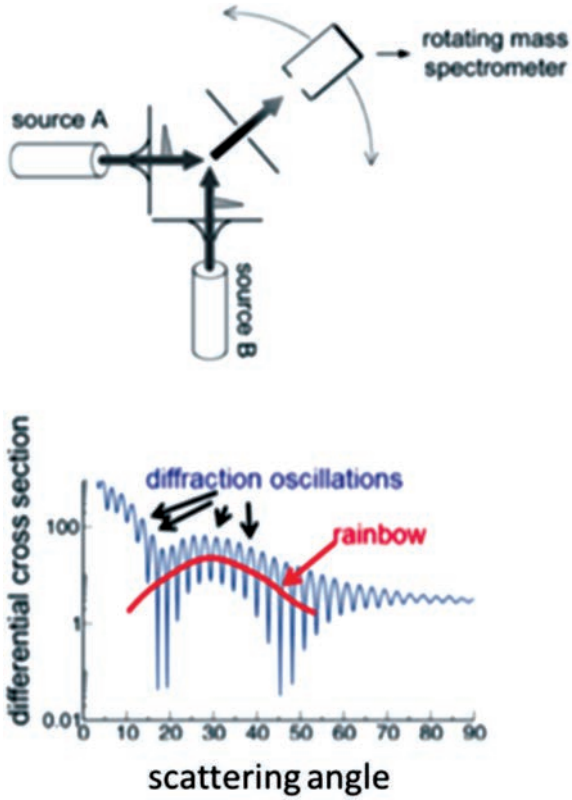


Fig. 2. The apparatus for the realization of differential scattering experiments. The velocity plot shows the quantum interference pattern that can be observed in this kind of experiments due to diffraction oscillations and to the rainbow effect (Adapted from Ref. 38).

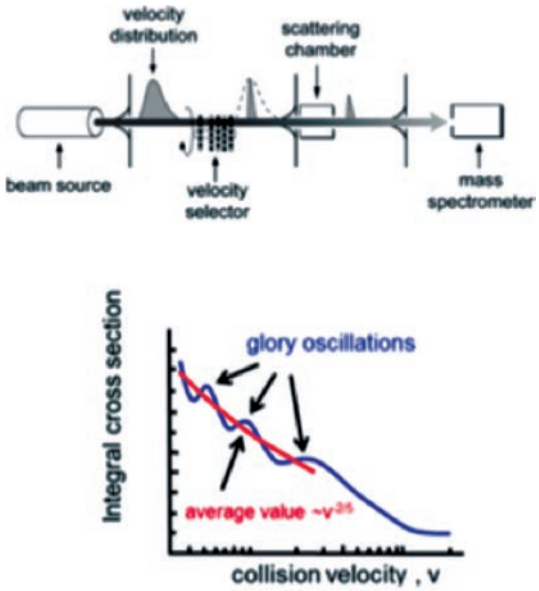


Fig. 3. A typical experimental setup for measuring integral cross sections by the attenuation of a molecular beam at selected velocities by a target gas in the scattering chamber. The plot shows glory oscillations superimposed to an average velocity dependence $v^{-2/5}$ due to the R^{-6} dependence of long-range interactions (Adapted from Ref. 38).

consisting of two crossed molecular beams and a rotating detector, for differential cross section measurements. Under high angular and energy resolution conditions, it permits the manifestation of rainbow and diffraction quantum interference effects, in the angular dependence of the differential cross sections.

In Fig. 3, we show an apparatus for the measurement of the integral cross sections as a function of the collision velocity, consisting of a molecular beam, velocity selected by a mechanical device consisting of a series of rotating slotted disks, of a scattering chamber and of a quadrupole mass spectrometer as a detector. This type of measurements exhibit, under favorable conditions, quantum interference phenomena that are given the names of analogous optical phenomena. In particular, diffraction and rainbow patterns are a manifestation of the rise of repulsive walls and of the strength of the attraction in the neighborhood of the potential wells; the glory quantum interference is instead a probe of the position and depth of the potential well. A chiral discrimination phenomenon is expected to be observed in the angular distribution of the fragments produced by collision of two identical enantiomers, RR, or opposite enantiomers, RS. Measurements of differential cross section, performed by the apparatus in Fig. 2, are suitable for this kind of enantiomeric selection.

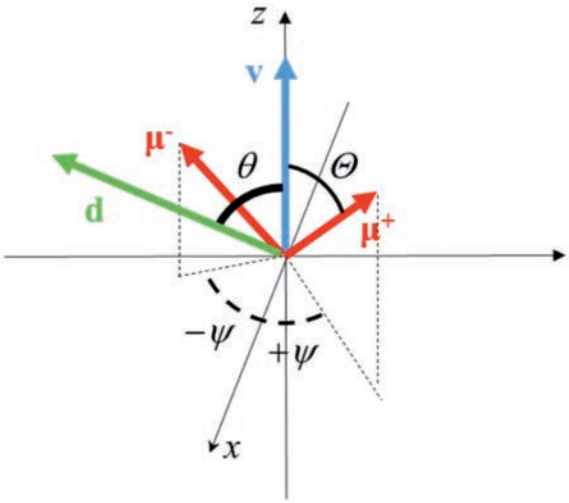
The apparatus in Fig. 3, suitable for measurements of integral cross section, permits to probe the different energy interaction between couple of enantiomers RR

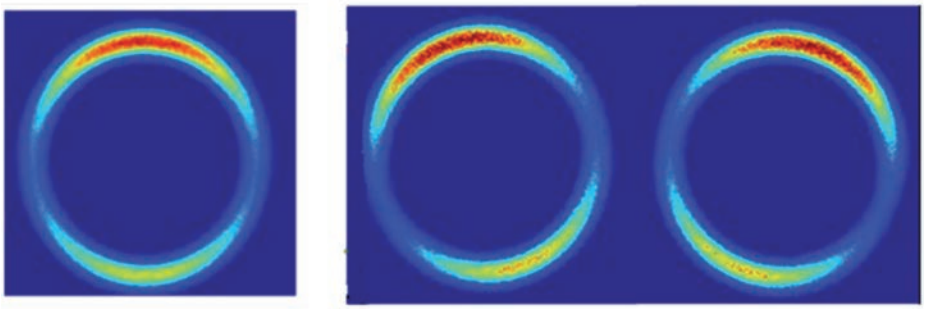
and RS. On this regard, we have estimated the interaction averaged over all the relative orientations of a couple of propylene oxide molecules RR and RS. Propylene oxide has been amply characterized by our group both from a theoretical and an experimental point of view. The average binding energy is estimated as about 3-4 kJ/mol at an equilibrium distance of 4-4.5 Å. Considering the information provided by spectroscopic measurements, we have estimated a difference in energy between RR ad RS couples of *ca.* 0.2 kJ/mol, that is about 5% of the total interaction energy. Ongoing experiments have been carried out involving propylene oxide. Additionally, for this molecule double ionization (valence shell) thresholds have been recently measured by synchrotron radiation [40].

4. *Chirality discrimination in photodissociation*

Enantioselective photodissociation experiments are performed on molecules oriented by an electrostatic hexapole, combined with the ion photofragment imaging detection technique. The photodissociation is induced by a linearly polarized laser, which is a non chiral source, but the aim is to point out the role of the orientation in originating chiral discrimination. The interpretation of the chiral effect involved is visualized by a semiclassical vector scheme in the electric dipole approximation in the molecular (body fixed) reference frame *xyz* (Figure 4, upper panel). The vectors to be considered are the velocity of the photofragments **v**, that identifies with the *z*-axis, the transition dipole moment $\boldsymbol{\mu}$ and the permanent electric dipole moment **d**. The angle θ between **v** and **d** has range $0 \leq \theta \leq \pi$ and the angle Θ between vectors **v** and $\boldsymbol{\mu}$ has also range $0 \leq \Theta \leq \pi$, while the angle ψ, given by the intersection of the *x*-axis with the projection of $\boldsymbol{\mu}$ onto the *xy*-plane, has range $0 \leq \psi < 2\pi$. Achiral molecules do not distinguish the sign of ψ, while for chiral molecules, a symmetry breaking occurs and the sign of ψ is characteristic of a specific enantiomer. It is important to note that the sign of ψ can be determined from the photofragment angular distribution of oriented (chiral) molecules via linearly polarized photolysis light. Prerequisite is that the three vectors must have a three-dimensional arrangement. It can be shown that, under sliced imaging conditions, θ and ψ can be determined from specific light polarization and orienting field arrangement.

In Figure 4 (lower panel), we report the simulation of the photofragment angular distribution obtained by ion imaging for a prototypical chiral molecule. A racemic mixture, as well as an achiral molecule, gives a symmetric distribution of the photofragments [41]. On the contrary, the separate enantiomers give an asymmetric distribution, characteristic of the corresponding mirror form. Recent experiments of enantioselective photodissociation involved the hexapole oriented 2-bromobutane [42-44].





Achiral molecule or racemic mixture

Separate enantiomers

Fig. 4. The upper panel reports the vectors and the angular coordinates that describe the angular distribution of the photofragment in the *xyz* Cartesian coordinate reference frame. The origin of the axes is the center-of-mass of the fragment, the *z*-axis is parallel to the direction of the velocity recoil vector **v** and the permanent dipole moment vector **d** is coplanar to the *xz*-plane. The angle between **v** and **d** is denoted by θ ($0 \leq \theta \leq \pi$), while the angle between **v** and **μ** is indicated by Θ ($0 \leq \Theta \leq \pi$). The **μ** vectors are indicated by the superscripts + and – that correspond to the enantiomers. The directions of $\boldsymbol{\mu}^+$ and $\boldsymbol{\mu}^-$, as well as the sign of ψ, the angle between the *x*-axis and the projection of **μ** on the *xy*-plane ψ ($0 \leq \psi < 2\pi$), are specific for each enantiomer. (Lower panel) In the left, we report the photofragment angular distribution of an achiral molecule, or similarly of a racemic mixture. In the right, the photofragment angular distributions given by separate enantiomers (Adapted from Ref. 41).

5. *Concluding remarks*

We have provided an account of molecular chirality manifestations in molecular beam experiments and the corresponding theoretical modeling. Chiral effects are expected to show up in the intermolecular interactions involving homo- and hetero-chiral molecular pairs and in the collision observables, where molecular alignment can arguably highlight such role of the stereodynamics. In dissociation experiments photoinitiated by linearly polarized laser, being a non-chiral source, molecular orientation is a fundamental prerequisite for the observation of chiral effects.

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