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Observed Molecular Alignment in Gaseous Streams and Possible Chiral Effects in Vortices and in Surface Scattering

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Abstract Extensive work in this laboratory has been devoted to the study of intermolecular interactions from scattering experiments, in order to provide ingredients for modelling forces acting in systems involving hydrocarbons, the components of atmospheres, and water. Our detection of aligned oxygen in gaseous streams and further evidence on simple molecules has been extended to benzene and various hydrocarbons. Chiral effects can be seen in the differential scattering of oriented molecules, in particular from surfaces. It is pointed out that it may be of pre-biotical interest that we focus on possible mechanisms for chiral bio-stereochemistry of oriented reactants, for example when flowing in atmospheres of rotating bodies, specifically the planet earth, as well as in vortex motions of celestial objects. Molecular dynamics simulations and experimental verifications are in progress.

Keywords molecular alignment · supersonic seeded molecular beams · vortices · homochirality

Introduction

In the recent discussions of the origin of homochirality in biology many previously advanced hypotheses are under scrutiny and none has yet received a global consensus. Evidence of the role of circular polarized light and in general of magnetic and electric fields, although experimentally demonstrated, appears circumstantial, because intensity of such fields has not been proved to be sufficient to induce substantial effects in the production of a specific enantiomer of a chiral species. For a review, see Avalos et al. (1998), and also Rikken and Raupach (2000) for asymmetric synthesis. The latest experimental observations [see, for example Stranges et al. (2005)] of dichroic effects in photoionization required very intense circularly polarized synchrotron radiation, probably

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not available in nature. Recent investigations of the origin of asymmetry based on accurate quantum chemical calculations have also shown that parity violation due to weak forces leads to extremely small energy difference for enantiomers (see the review by Quack (2002), the latest paper by Faglioni et al. (2005), and references therein).

The present contribution is a move in an alternative direction. Chiral separation can arise in vortices, and is exploited in centrifugal separation chromatography. These phenomena occur in the liquid phases. Our recent experimental investigation proves interesting alignment and orientation effects in the gas phase, simply due to microscopic events– namely molecular collisions naturally occurring in streams, typically when in a gaseous mixture a "heavier" molecular component is seeded in a lighter one. These observations are briefly reviewed in the first part of this paper. The second part investigates the possibility that similar microscopic events occurring in vortices and surface scattering may lead to chiral discrimination. Some molecular dynamics arguments are given, awaiting for detailed model calculations. Most interestingly, experimental demonstrations appear to be within reach both for vortex motion (Su, private communication) and for scattering experiments at surfaces.

Alignment in Streams

In this section we will illustrate the state-of-the-art with examples from this laboratory for alignment in gaseous streams and then proceed with an overview of current progress in experimental and theoretical approaches and of further perspectives. Some recent achievements in experimental techniques for controlling the spatial orientation of molecules [see the reviews Aquilanti (2005); Aquilanti et al. (2005)] represent, for the time being, tools for investigations of the basic mechanisms, but perspectives are open to also exploit them for applied purposes in chemical stereodynamics.

Aligning and orienting molecules

Recent papers (Pirani et al. 2001, 2003) provide our starting point for this account of advances in the production of intense and continuous beams of aligned molecules, demonstrating that in the prototypical case of a seeded supersonic expansion of a beam of the disc-shaped molecule benzene, besides acceleration and cooling, orientation of the molecular plane also occurs because of the anisotropy of the intermolecular forces which govern collisions. Previous studies on the collisional alignment of the rotational angular momentum of diatomic molecules regarded O_2, for which the effect was probed by magnetic analysis (Aquilanti et al. 1994, 1995) and N_2, for which the probe was molecular beam scattering (Aquilanti et al. 1997). Extensions to other hydrocarbons, particularly ethylene, have been also demonstrated (Cappelletti et al. 2006).

Up to now, we have been using terms like orientation and alignment as synonyms. According to current usage, we should consistently use alignment here, leaving orientation only for cases where one also specifies "heads" or "tails" spatial features of a molecule. However, "alignment of a molecular plane" is somewhat contrary to common linguistic usage and we will often employ "orientation" to obtain a more immediate picture of the phenomenon. We refer to collisional alignment techniques as "natural" ones, as compared to those where external fields induce a "forced" alignment. We mention the focusing in electric fields through the Stark effect, which can be either second order for linear molecules or first order for symmetric top molecules (the latter stronger than the former), the use of polarized absorption (limited to optically favorable transitions in the molecular manifold), the *brute force* techniques, which use strong electrical or magnetic fields and are applicable only to rotationally relaxed molecules with permanent electric or magnetic dipole moments, and the alignment in intense non-resonant laser fields. Further details and updated developments toward dramatic improvement in intensity will be referred to in the next section, but interest for the situation of naturally occurring fields in uncertain.

Natural alignment in supersonic seeded beams

A natural and effective molecular alignment technique involves microscopic collisions in environments exhibiting anisotropic velocity distributions, such as supersonic expansions of seeded molecular beams. Historically, this phenomenon was suggested long ago to occur in transport processes but it was observed much later and shown to be less trivial and much more interesting. Simple inorganic molecules, like Na_2, Li_2, I_2, and CO_2, had been found to align their rotational angular momentum in supersonic expansions when seeded with lighter carriers. Considerable efforts were devoted to the characterization of the dependence of the phenomenon on the probed rotational levels and on the beam source conditions, such as the stagnation pressure, the gas carrier composition, and the angular displacement off the molecular beam axis.

Aquilanti et al. (1994), by measuring the variation of the paramagnetism of O_2 in continuous supersonic seeded molecular beams of molecular oxygen relaxed in the lowest rotovibrational states reported the first experimental evidence of the strong dependence of the alignment on the final molecular speed. Further probing of alignment by scattering cross-section measurements, performed downstream of the beam source and using as projectiles velocity selected O_2− and N_2−seeded molecular beams and rare gas as targets (Aquilanti et al. 1997), confirmed the correlation between molecular alignment and molecular velocity and allowed both an accurate determination of the involved interaction potential energy surfaces and characterization of the collisional dynamics of aligned molecules. The quantum mechanical theory is outlined by Aquilanti et al. (1999). These experiments suggested that measurements of anisotropy effects in the scattering cross-sections, combined with a proper velocity selection of the molecular beams, are an alternative source of information on the molecular alignment degree if the topography of the potential energy surface and details of the involved collisional dynamics are available.

Recently (Pirani et al. 2001, 2003), our interest has been addressed to the demonstration that the disk-shaped benzene molecule in supersonic seeded molecular beams would act similarly. Note that in this case the alignment of the rotational angular momentum corresponds to a preferential orientation of the molecular plane along a particular direction. Benzene is a favorite target of organic chemists for studies of steric effects, so we could imagine a wide range of applications for an oriented benzene molecular beam, in particular for investigation of the stereodynamics of elastic, inelastic, and reactive events. The probing of the orientation has been carried out through two complementary experiments – direct IR laser absorption and molecular beam scattering.

Other methods and applications

Several molecular beam techniques to force the molecular orientation have been developed using electrostatic or optical methods. References have been listed in Aquilanti et al.

(2005), where progress is described on how to improve hexapole electrostatic state-selectors, which are frequently employed to study the stereodynamics in chemical reactivity, such as reactive gas-phase scattering, surface scattering, photodissociation, and electron scattering. Applications have also been listed in Aquilanti et al. (2005).

In a recent experiment (Vattuone et al. 2004) the sticking of ethylene molecules on a 001 Ag surface, at 80 K and saturated with O_2 molecules, has been studied as a function of the degree of alignment of ethylene as produced in a velocity selected supersonic seeded beam. It has been found that the sticking coefficient strongly depends on such an alignment: when the molecules arrive on the surface rotating “helycopter”-like, they have a sticking tendency about 30% larger than that when they arrive rotating “cartweel”-like. This is a new twist in nano-catalysis, namely steric control at the level of microscopic elementary processes: this is anticipated to make possible practical applications in chemistry, and so will necessitate further research effort at the nano-scale.

Chiral Scattering of Oriented Molecules in Vortices and at Surfaces

A link to the previous section is suggested from the recent astrophysical discovery of aromatic molecules, particularly benzene (Cernicharo et al. 2001): this supports the study of their role in building up species of prospective biochemical interest. So our detection of aligned benzene and hydrocarbons in gaseous streams points out that as our future work-plan we focus on possible mechanisms for chiral biostereochemistry (or indeed photobiology) of oriented reactants – for example when flowing in atmospheres of rotating bodies, specifically the planet earth – and particularly investigate vortices, where under rarefied gas dynamics conditions, not only alignment and orientation can be produced, but possibly even chirality discrimination (Lee et al. 2004, and private communication).

A two dimensional analogue to illustrate observations detailed in the previous sections can be pointed out. Logs floating down a river would show up on the average aligned along the stream. Dynamically, they would be modeled by a linear object with two equal moments of inertia, and the third one zero. Alignment in streams would occur for an object whose moments of inertia would be those a planar lamina (two moments of inertia adding up to the third one), idealized as an isosceles triangle (Aquilanti et al. 2000). A scalene triangle is chiral in the plane: a stream of floating logs would not discriminate enantiomers, but if the river bends, it might. And it will do it differently if it bends to the right or to the left! In a vortex, adding another dimension to the problem, a three dimensional physical objects with three different moments of inertia – idealized as a fully irregular tetrahedron – may be discriminated in the two possible enantiomeric forms.

Ray et al. (1999) had shown that when chiral molecules are given a specific orientation in a film, asymmetry results for the scattering by polarized electrons. More recently Kim et al. (2005) studied photoemission by absorbed chiral molecules. As seen in “Alignment in Streams”, Vattuone et al. (2004) and Gerbi et al. (2005a,b) demonstrate stereodynamic effects in scattering from surfaces of molecules aligned according to the technique described in the previous section.

Among the possibility of chiral physical fields, circularly polarized photons, and the magnetochiral effect induced by the magnetic field and unpolarized light, have been shown to be enantioselective in photochemical reactions. But in general translation–rotation motions are true chiral force fields: recently, liquid vortex motions have been shown to induce chiral discrimination in the formation of mesophase aggregates of achiral porphyrins (Ribó et al. 2001).

Busalla et al. (1999) have given a theoretical proof that in collisions between unpolarized projectiles and chiral molecules, the differential cross-sections for a molecule and its enantiomer differ if the molecules are oriented. They also showed (Musigmann et al. 2001a, b) that left- and right-handed molecules can scatter unpolarized electrons differently if a chiral framework is provided by at least three non-coplanar polar vectors defined in the collision processes (see also Thompson and Blum 2000; Thompson 2004). This concept extended to translation–rotation collision conditions provides a molecular mechanism for chirality generation. Taking the seeded supersonic beams of the previous section as experimental evidence, inside a vortex, the major gas component is seen to drive the seeded molecules in the form of a directed flow. Classical trajectory calculations (Lee et al. 2004) show that a seeded beam of an organic molecule (1-bromo-2-chloroethane with argon) is oriented such that the bromo-end is pointing in the Ar flow direction. If it is now considered that the oriented molecules are colliding within a vortex, with their velocity direction being perpendicular to the orientation of the molecules, the macroscopic translation–rotational motion would set up a chirality generating environment. Su et al. (to be published) show by molecular dynamics calculations that preferential excitation of the conformational motion can come into play, most effectively by applying a torque along the C–C bond to the chloro-end, the farthest fragment from the mass center of molecules – for example, through collisions with a surface. This may result in a preferential accumulation of one of the rotamers in the properly screw sense of motion, leading to observations of molecular chirality enrichment (Lee et al. unpublished).

Conclusion

Macroscopic translation–rotational motion could induce molecular chirality through the processes of molecular orientation and preferential energy transfer in the differential scattering of enantiomers. It will be of interest to study the molecular dynamics and the scaling with physical sizes of vortices and with the type of molecules in a stream. A particularly fascinating scenario is in the formation of a typical low-mass star, such as our solar system (Hartmann 2000). In the process of stellar accretion, a rotating stellar core is formed together with a co-rotating circumstellar disk. The disk accretion process would generate highly collimated bipolar jets/winds in the direction perpendicular to the disk mimicking a seeded molecular beam situation, according to the discussion in "Alignment in Streams". These translation–rotational jets/winds arising from the rotating disk surface, and the accompanying slower molecular flows, would collide with the matter which surround the disk, and this situation contains the basic ingredients for the generation of chiral matter. Su et al. (private communication), providing experimental evidence of the basic mechanism in laboratory gas flows are led to suggest that during stellar formation, chirality-enriched matter of opposite sign could be separately generated and distributed in the south and north regions of the stellar disk. In the final formation of planets such as the earth, it is plausible that large portions of the early planet could be dominated by just one type of chirality-enriched matter, setting the stage for homochirality at the emergence of life. Indeed, the Coriolis forces which act in the terrestrial atmosphere (Gladyshev 1992) lead to tornadoes with opposite chiralities in the northern and southern hemispheres. Present knowledge of possible chirality in streams is in its infancy and has to be further investigated to prove or disprove any role in prebiotic issues. In the agenda for future work, this paper suggests that we list study of properties of scattering by aligned or oriented chiral molecules and accompanying molecular dynamics simulations.

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