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Stereodynamical effects by anisotropic intermolecular forces

Abstract – Alignment and/or orientation of molecules (i.e. non-statistical spatial distributions of their rotational angular momenta, their molecular axes and/or their molecular planes) can be naturally induced during two body collisions in gas phase. The nature and strength of the intermolecular forces involved, and their anisotropies govern the collision dynamics and a deep understanding of the physical mechanisms underlying collisional alignment/orientation is crucial to control the stereodynamics of elementary chemical-physical processes. By using different experimental techniques and theoretical methodologies the effect of polarization on elementary processes involving neutral and ionic species are presented and discussed for both weakly and strongly interacting systems.

1. Introduction

Electric and magnetic field gradients, arising from anisotropic intermolecular forces, can induce molecular polarization, *i.e.* alignment and/or orientation of a molecule as a consequence of collisions with other atoms or molecules. A deep knowledge of these phenomena, today still not fully understood, is of general relevance to control the stereodynamics of elementary chemical-physical processes, occurring both in gaseous and condensed phases and involving neutral and ionic species (Vattuone *et al.* 2010). The possibility of aligning/orienting molecules in gaseous streams by virtue of collisions may have some implications in understanding the origin of

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chiral discrimination and chiral selectivity emerging in vortices formed both in the liquid and in the gas phase (Lombardi *et al.* 2018 and references therein; Su *et al.* 2013). It is intriguing to think that polarization phenomena involving chiral molecules might have implications for the emergence of homochirality in the Universe and connections might be proposed with vortex generation in the atmospheres of rotating planets and satellites or in the protoplanetary disk phase of stellar formation.

This short review paper reports on results obtained, by exploiting an integrated experimental-theoretical approach, within a long-standing collaboration between the research groups in Perugia and Trento. By combining information obtained with different techniques and experimental set-ups, it will be highlighted how molecular polarization, induced in a *natural way* by anisotropic forces, plays a role on the stere-odynamics of reactive and non-reactive collisions.

2. Molecular alignment by weak anisotropic forces

Several experimental findings suggest that, when only weak van der Waals forces are operative among the colliding partners, molecular alignment is the result of a combined effect of several elastic/inelastic collisions occurring along preferential directions in environments where anisotropic velocity distributions are operative. It is the case of supersonic expansions leading to the formation of *seeded molecular beams*, where hundreds of collisions among seeded molecules and lighter carrier atoms occur preferentially in the forward direction of the expansion. Two limiting collision regimes can be identified in the expansion zone, with increasing distance from the nozzle, where different relative collision velocities (defined as *velocity slip*) and gas densities are present (see top part of Figure 1). Molecules emerging from the nozzle suffer hundreds of collisions (both elastic and inelastic and at different impact parameters) and are accelerated, focused in the forward direction and aligned, as pictorially shown in the central and bottom part of Figure 1.

Two different experimental ways to probe the alignment degree far from the beam source have been used in the Perugia laboratory: the first one exploits the measure of the beam transmittance across a Stern-Gerlach magnetic selector and it is applicable only to paramagnetic molecules such as O_2 (Aquilanti *et al.* 1994, 1995a, b, 1998). The second one, of more general applicability, involves measurements of beam intensity attenuation in scattering experiments with a spherical target (Aquilanti *et al.* 1997).

The magnetic analysis performed on O_2 seeded beams has shown that molecules achieve a high and anomalous paramagnetism, related to a non-statistical distribution of their magnetic sublevels. The paramagnetic degree is found to increase with the final speed achieved by the molecules within the same velocity distribution, and with the pressure employed in the source (Aquilanti *et al.* 1994, 1995a). In other words, molecules flying in the head of the molecular beam, with intermediate and high supersonic character, exhibit the highest polarization degree. In addition, it was sug-



Fig. 1. *Center*: a pictorial view of the formation of a skimmed molecular beam by expansion of a gas mixture through a nozzle. *Top*: dependence of the *velocity slip* with the nozzle distance. The vertical dashed line defines the two different limiting regions: at short distance from the nozzles many body elastic and inelastic collisions lead to molecular rotational excitation and relaxation. At larger distances only elastic and inelastic processes at low energy (rotational relaxation) can occur, producing the sequence of events illustrated in the bottom part. *Bottom*: effect of collisions at different impact parameters b. Collisions at large inpact parameters (1 and 6) are mostly elastic and lead to focusing in the forward direction; collisions at intermediate b (2 and 5) lead bending of the rotational plane (promoting alignment in the «edge-on» configuration); collisions at small b (3 and 4) lead to acceleration and relaxation.

gested that a high simultaneous/combined polarization of **K** (the rotational angular momentum) and **S** (the electronic spin angular momentum) is achieved by faster molecules (Aquilanti *et al.* 1999). A key for understanding the origin of such effect is to consider that during the collision, the intermolecular electric field strength is sufficient to decouple **K** from **S** (which are coupled to give the spin-rotational angular momentum **J** in the isolated O_2 molecule), and its anisotropy (or gradient) tends to form states with *zero helicity*, that is exhibiting *zero projection* of **K** along the flying direction. Under such conditions, the unique quantization axis for **S** is the direction of the orbital angular momentum of the collision complex. After the collision **K** couples again with **S** and a polarization transfer between **K** and **S** can occur.

The extent of molecular alignment has been found to depend on the geometric features of the nozzle, on the gas density and on the resolution conditions adopted in the detection of aligned molecules (Aquilanti et al. 1994, 1995a, b, 1997, 1998, 1999), but it turned out to be nearly independent on the type of lighter carrier species. The latter finding led to the introduction of the *reduced speed* (i.e. the ratio between the selected molecular velocity v and the peak velocity of the molecular beam v_x) as a proper scaling factor for the alignment degree. Hence, exploiting the velocity selection technique, it has been possible to sample in a controlled way molecules flying at the same speed but having a different alignment degree, as detailed in panel a) of Figure 2 (Aquilanti et al. 1994, 1995a). By combining velocity selection with scattering experiments it was possible to measure not only velocity dependences of the cross section for projectile molecules flying with the same reduced speed, but also of the cross section anisotropy due to the change of the speed ratio. Results for the O_2 -Kr system are shown in panel b) of Figure 2 (Aquilanti et al, 1998). Scattering experiments were particularly useful in the case of diamagnetic N2 projectiles (Aquilanti et al. 1997).

An integrated investigation exploiting scattering and spectroscopic probes has been performed on some seeded beams of hydrocarbon molecules (Pirani *et al.* 2001, 2003), while other cases of molecular polarization have been investigated with different techniques, as discussed in (Aquilanti *et al.* 2005).

3. Molecular orientation by intermediate strength forces

Molecular orientation controlled by anisotropic intermolecular forces of intermediate strength manifests even in single collision events if the molecules involved are in low lying rotational states. Orientation can be achieved in the presence of a permanent dipole moment for the molecular target, and the water molecule, having a large dipole moment but an electronic polarizability very close to that of O_2 and Ar, is the ideal candidate to investigate the role of different contributions to anisotropic intermolecular interactions, with special reference to intermolecular hydrogen bonds, and their effects on collision dynamics properties (Cappelletti *et al.* 2012). Even working with rotationally hot and randomly oriented projectile-target



Fig. 2. *a*): velocity distributions (solid lines) of O_2 supersonic beams seeded in increasingly lighter mixtures of atomic carriers: Ne (blue), He (green) and a Ne+He mixture (red). The dashed lines represent the speed dependence of the alignment for molecules flying within the same velocity distribution. By probing the tail of the Ne+He seeded beam (red square) or the head of the Ne seeded beam (blue square) O_2 molecules having the same speed but different alignment degree can be selected. *b*): integral cross sections for scattering of O_2 molecules having different *reduced speed* (hence different alignment degrees) and using Kr as the spherical target.

molecule pairs, there is clear evidence that an electrostatic interaction contribution is operative, arising from the partial polarization achieved by water molecules during the collisions (Roncaratti *et al.* 2014 a, b). The anisotropic intermolecular potential between two water molecules is sufficiently strong to couple their permanent dipole moments within the field gradient, thus transforming *free rotations* into *pendular states,* a particular case of bending motion. H₂O molecules with very similar rotational periods and in low lying rotational states are more efficiently coupled, in what has been pictorially described as a *synchronized dance of water molecules* (Roncaratti *et al.* 2014 a, b).

4. Molecular orientation by strong intermolecular forces

Molecular orientation effects become dominant in each collision events when the anisotropic intermolecular forces have high intensities. Such a situation can occur under an ample variety of conditions, but here we will focus on collisions involving charged species. Physical and chemical processes involving ions occur in many gaseous and plasma environments (e.g. ionospheres of planets and satellites, interstellar medium, laboratory plasmas for technological applications), where ion-molecule reactions participate in the balance and redistribution of charges in the above-mentioned systems, as well as to the synthesis/destruction of chemical species. In the case of ion-molecule reactions, alignment/orientation is a general phenomenon due the large electric fields generated by the charged particle. Polarization might lead to stereodynamic effects that can either enhance or suppress reactivity. The former effect is achieved when alignment/orientation drives the collision complex into the most appropriate configurations for reaction (see the enhanced reactivity at low collision energies in the $H_2^+ + H_2 \rightarrow H_3^+ + H$ reaction, Allmendinger *et al.* 2016). The latter occurs when long-range interaction potentials reorient the reacting couple either in a non-reactive or in a configuration unfavorable for reaction, as in the case of the H-atom transfer reaction between H, and H₂O⁺, where reorientation of H₂O⁺, facilitated by rotational excitation, is necessary to promote reactivity (Li et al. 2014). Another example is represented by the positive temperature dependence shown in the rate constants of the barrierless and exothermic charge exchange reactions between Ar⁺ and N₂⁺ ions and diatomic interhalogen molecules ICl and ClF (Shuman et al. 2017). The extent of long-range ion-molecule interaction potentials are also at the basis of the effects observed on bimolecular reactivity by different rotational isomers (conformers) of a polyatomic molecule in the gas phase (Chang et al. 2013; Rösch et al. 2014).

Collisions with He⁺ are an important pathway for the decomposition of «complex organic molecules» (COMs, i.e. molecules containing at least six atoms) in the interstellar medium. Within this framework, we recently investigated charge transfer reactions of He⁺ with dimethyl ether CH₃OCH₃ (DME) and methylformate HCOOCH₃ (MF), two amongst the most abundant COMs with a prebiotic rele-



Fig. 3. *a*): Cut of the potential energy hypersurface (with the He⁺ ion confined in the plane defined by the C-O-C atoms) for the entrance channel of the He⁺-DME system. *b*) Pictorial representation of the formation of a *pendular state* during collisions between He⁺ and DME: at large ion-neutral distances the molecule is rotating freely (left), while at shorter distances (right) the PES anisotropy is so prominent that free rotations are hampered and DME librates around the direction of preferential orientation; *c*) electron density distribution for one of the inner valence molecular orbitals of DME involved in the electron transfer process with He⁺.

vance for their capability of acting as building blocks for sugars and biopolymers (Balucani *et al.* 2015). Using the Guided Ion Beam Mass Spectrometer in Trento reactive cross sections and branching ratios (BRs) as a function of the collision energy have been measured (Cernuto *et al.* 2017, 2018). Due to the large dipole moments exhibited by the neutral collision partners the studied systems present large interaction anisotropies that can induce strong steroedynamic effects and influence the outcome of reactive collisions. The experimental evidence is that electron exchange processes are completely dissociative, leading to extensive fragmentation of the neutral partner, and cross section trends with collision energies are at odds

with those expected from simple *capture models*. By investigating the nature of the non-adiabatic transitions between the reactant and product potential energy surfaces using an improved Landau-Zener model, we were able to identify three critical elements at the basis of such discrepancy: the strong anisotropy of the potential energy hypersurface (PES) in the entrance channel, the crossings among entrance and exit PESs and the symmetry of the electron density distributions of the molecular orbitals involved in the electron transfer to He⁺ (Cernuto et al. 2017, 2018). The presence of deep potential wells for selected configurations of the reacting couple induces pronounced orientations of the polar neutrals in the electric field generated by the cation (*i.e.* formation of *pendular states* in which the molecule librates around a preferential direction), thus channelling most of the molecules in narrow angular cones confined around the most attractive configurations of the interacting systems. A cut of the PES for the He⁺-DME system is reported in panel *a*) of Figure 3, while a pictorial view of the formation of *pendular states* is shown in panel b) of the same Figure. The crossing positions among entrance and exit PESs force He⁺ to capture an electron from an inner valence molecular orbital of the organic molecules, thus producing quickly dissociating molecular cations in highly excited states. The symmetry of the electron density distribution of the molecular orbitals from which the electron is removed affects the probability of electron transfer to He⁺. For both DME and MF the overlap integral between the orbitals involved in the electron exchange is unfavourable (see panel c) of Figure 3 for the He⁺-DME case), thus originating the paradox that the most attractive geometry is the least efficient for charge transfer.

As general conclusion, it is proper to stress that molecular polarization effects, induced in all investigated cases by anisotropic intermolecular forces of different strength, tend to become more prominent under sub-thermal conditions. Hence they should be properly taken into account when modelling non-reactive as well as reactive systems in low temperature environments such as the interstellar medium and planetary atmospheres.

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