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Cooling and alignment of ethylene molecules in supersonic seeded expansions: diagnostic and application to gas phase and surface scattering experiments

Collisional alignment

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Abstract. Rotational cooling and collisional alignment of ethylene molecules is induced by seeding effects in supersonic expansions with lighter gas carriers such as He and Ne. The dependencies of the degree of alignment on the rotational state, on the final speed of the molecules and on the diffusion angular cone have been characterized by coupling two different experimental methodologies. An application to surface scattering is then demonstrated by measuring stereo-dynamical effect in the adsorption on metallic surfaces.

PACS. 39.10.+j Atomic and molecular beam sources and techniques – 68.49.Df Molecule scattering from surfaces (energy transfer, resonances, trapping)

1 Introduction

When diluted gaseous mixtures expand into vacuum through holes having diameters greater than kinetic mean free paths, the heavier components are accelerated to supersonic speeds higher than for pure gases: this ‘seeding’ phenomenon leads to cooling of molecular rotations and also, in favorable cases, to spatial alignment of the rotational angular momentum. The cooling and alignment of molecular rotations are the results of several elastic and inelastic collisions between seeded molecules and faster carriers, probing a wide range of orbital angular momenta (or classically of impact parameters) and collision energies.

A striking correlation between velocity and alignment degree of molecules emerging from supersonic seeded expansions has been first demonstrated experimentally for continuous molecular beam of O_2 [1] and successively observed in continuous beam of N_2 [2], pulsed beam of CO [3], drifted N_2^+ in He [4] and continuous beams of benzene [5,6]. Besides the rich phenomenology evidenced in the above cases, there is a rather general agreement on the observation that final speed, rotational state and alignment degree achieved by seeded molecules in the *collision free* region after the supersonic seeded expansion, must depend critically on the mass difference and on the interaction potential anisotropy of the seed–carrier pair, on the density and statistic of the rotational levels of the seeded molecules and on the range of impact parameters probed during the collisions in both the *continuous flow* and *transition* regions of the expansion.

A detailed quantum mechanical investigation of the stereo-dynamics of the phenomenon, conducted at a single collision level, suggests [7] that the basic quantity which determines the propensity to generate a certain molecular alignment is the state-to-state differential cross-section in the forward direction of the laboratory reference frame. For this reason the extent of the alignment is expected to depend markedly on the acceptance of angular cone probed in the forward direction of the expansion. So that, when collimating slits are used to collect a molecular beam emerging from the expansion region and to detect it further downstream, the angular resolution of the apparatus will critically determine the outcome of the experiment. Similarly, if a velocity (or energy) analysis is carried out on the formed molecular beam, the velocity resolution will also be critical. However, up to date there are no

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apparatuses which enable to elucidate in a single experiment the role of all the variables mentioned above.

We focus here on the case of the ethylene molecule and present the joint effort of three laboratories to characterize the behavior of continuous supersonic seeded expansions of C_2H_4 and the stereo-dynamics associated with its successive interactions with gas phase species and solid surface targets, as they may be induced downstream in the formed molecular beam.

Specifically, an IR absorption experiment is described in Sections 2.2 and 3.1 which allows the characterization of the rotational state dependence of the alignment degree. Second, a gas phase scattering experiment is described in Sections 2.3 and 3.2, providing the experimental evidence that the alignment degree depends on the final speed of the molecules. Finally, as shown in Sections 2.4 and 3.3, the features of ethylene molecular beam, characterized in the two previous experiments, are exploited in the study of the stereodynamics of ethylene adsorption on a metal surface.

2 Experimental methods

2.1 The molecular beam source

For a meaningful interpretation of the results the three experiments have been set-up to employ a molecular beam source operating under very similar conditions. So that, in all the present apparatuses a continuous supersonic seeded molecular beam emerges from the source and expands through a set of differentially pumped vacuum chambers where it undergoes collimation and velocity analysis. Finally it is detected by means of different techniques.

Gaseous mixtures of ethylene diluted in He or Ne ($\sim$2.5% $\div$ 5%), at total stagnation pressure P_0 in the range 1–2 bar have been expanded into vacuum through a sharp edged circular nozzle to produce continuous supersonic seeded molecular beams.

The nozzle diameter d used in the Perugia and Trento apparatus is $\sim$100 μm with a $P_0 \sim 1$ bar while in Genova the nozzle diameter is 80 μm with typical P_0 of $\sim$1.5 bar. In all cases the $P_0 \times d$ product is always in the range 8–12 mbar×cm. In all the apparatuses a conical skimmer, placed in front of the nozzle at a distance of $\sim$1 cm samples the central part of the emerging molecular beam.

The use of mixtures of carrier gases has been exploited to carry out scattering experiments in a wide range of collision energies. Typical velocity distributions of supersonic molecular beams of ethylene seeded in various gaseous mixtures, as measured in Perugia with a high resolution mechanical velocity selector, are reported in Figure 1: the FWHM (full width at half maximum) of the distributions is about 9% in all cases. This corresponds to a translational temperature of $\sim$3 K.

2.2 IR laser absorption experiment

The experimental set-up for the IR laser absorption experiment, operative in Trento, has been described in detail elsewhere [8]. A schematic representation is given in Figure 2.

Here, the molecular beam crosses perpendicularly an IR laser beam which can be polarized parallel ($\|$) or perpendicular ($\perp$) with respect to the beam propagation direction. The selective light absorption originates a signal A at the detector, a bolometer. Figure 2 shows the $A_\|$ and $A_\perp$ signals which can provide information on the degree of molecular alignment. The measurable difference between $A_\|$ and $A_\perp$ is related also to the choice of the involved molecular transition dipole. The probed IR transition at about 2990 cm^{-1} corresponds to the fundamental ν_{11} vibrational mode measured on a few J rotational states.

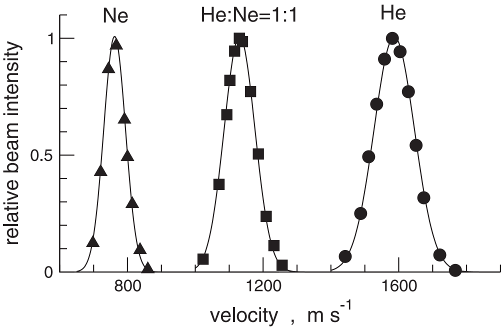

Fig. 1. Velocity distributions of ethylene continuous supersonic molecular beams seeded in various carrier gases.

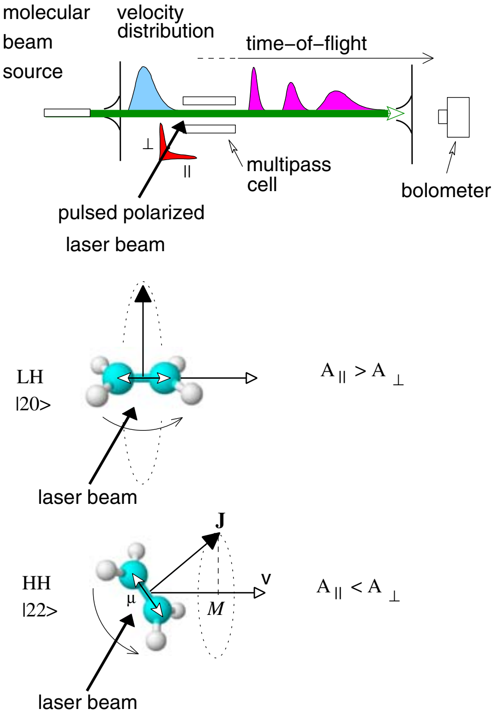

Fig. 2. The Trento molecular beam apparatus for IR laser absorption experiment. The rotational angular momentum **J** and its projection M along the beam propagation axis v are indicated. Typical low helicity (LH) and high helicity (HH) rotational states $|JM\rangle$ are pictorially illustrated for the $J = 2$ case with an indication of their propensity to absorb the polarized IR laser light.

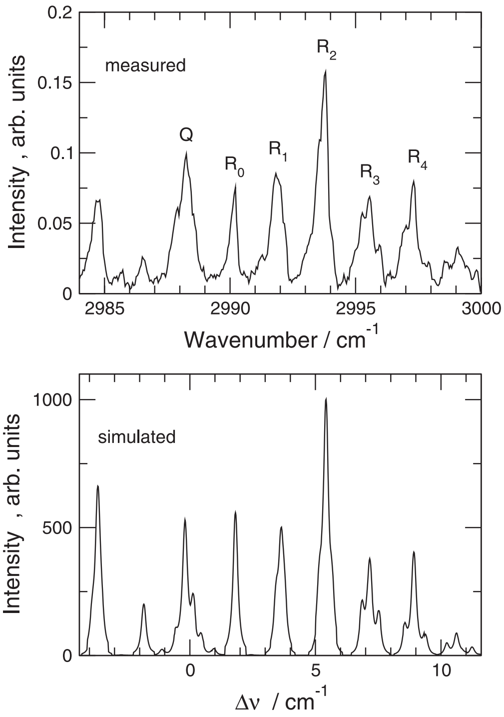

Fig. 3. Ethylene rotational spectrum simulated at 25 K and as measured on Trento experiment.

This transition arises from an asymmetric C–H excitation stretching and it is associated to a transition dipole moment μ lying along the C=C axis (see the white arrows in Fig. 2): in this case the anisotropy in the absorption can be directly related to the molecular alignment. The geometry of the experiment may also influence the observables: in the present case (laser beam transverse with respect to the expansion axis) it is expected to attenuate the anisotropy in the absorption.

The apparatus has been also used to monitor the rotational state distribution in the molecular beam. A comparison between measured and simulated [9] rotational spectra (see Fig. 3) provides the evidence that 2/3 of the population is in $J = 1$ and $J = 2$. An estimate of the rotational temperatures can also be given as reference and is ∼25 K.

2.3 Gas phase scattering experiment

The experimental set-up for the gas phase scattering experiment, operative in Perugia, has been described in detail elsewhere [2,6]. A schematic representation is given in Figure 4.

Here, the molecular beam is velocity analyzed by a high resolution (eight disks) mechanical velocity selector and, after a further collimation, scattered by a gas phase target contained into a scattering chamber maintained at low temperature (85 K). The molecular beam intensity is monitored by means of a quadrupole mass spectrometer and the measure of its attenuation due to collisions with the target gas, under high angular and velocity resolution conditions, allows the determination of the integral scattering cross-section, Q.

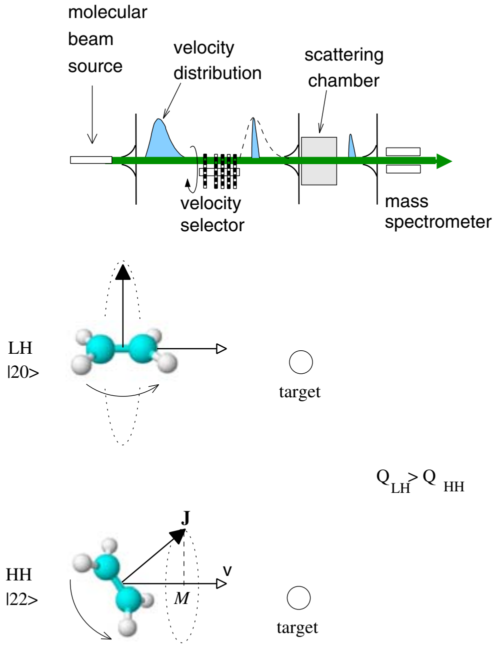

Fig. 4. The Perugia molecular beam apparatus for scattering cross-section, Q, measurements. Typically, for a low helicity state Q_{LH} is larger than for a high helicity state Q_{HH}.

Such an observable varies with the selected beam velocity and depends on the strength of the intermolecular interaction. The latter is anisotropic, so that the scattering cross-section depends on the molecular alignment degree (see Fig. 4). In order to obtain such an information an accurate knowledge of the interaction potential energy surface and correct treatment of the collisional dynamics of aligned molecules is required [2,10]. Although Q depends on an average of collisional events at various impact parameters, its measure involves the same symmetry of the expansion process. Therefore, as it will be shown in the following Section 3.2, it can provide important information on the alignment degree and on its dependence on the final velocity of the seeded molecules.

2.4 Surface scattering experiment

The experimental set-up for the surface scattering experiment, operative in Genova, has been described in detail elsewhere [11]. A schematic representation is given in Figure 5.

In this case the molecular beam is velocity analyzed by a two disk mechanical velocity selector, in the second stage of the molecular beam collimation [12]. This compact device has been developed to be easily inserted into the existing Genova apparatus [13] and even if it shows a lower velocity resolution with respect to the Perugia selector, it permits to separate molecules traveling in the fast tail (FT) from those moving in the slow tail (ST) of the velocity distribution. Furthermore, the two disk velocity

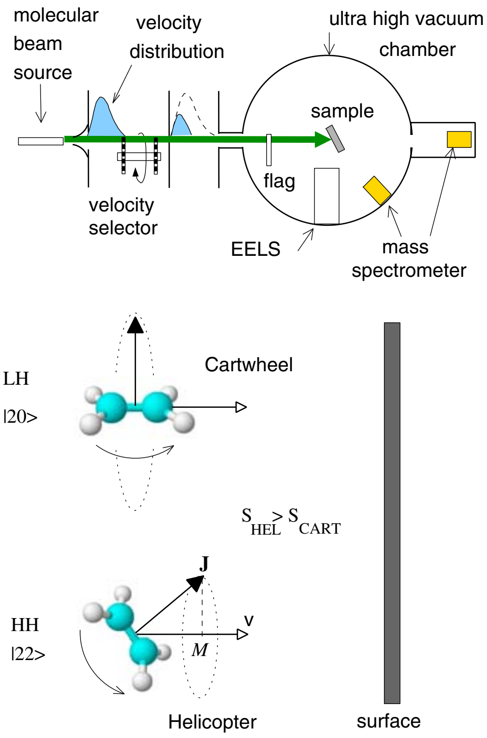

Fig. 5. The Genova apparatus for surface scattering experiments. LH and HH molecular states are referred to as cartwheel and helicopter classical motions, more appealing to describe the perpendicular approach to a surface. Under certain conditions, the sticking probability for helicopters, S_{HEL}, comes out to be larger than that for cartwheels, S_{CART}.

selector provides a high beam transmission, sufficient to perform sticking measurements. The latter are carried out by coupling the velocity selected supersonic beam with an Ultra High Vacuum (UHV) chamber (base pressure 2×10^{-10} mbar), where the sample is located. The quantitative information obtained in the Perugia experiment on the velocity dependence of the ethylene alignment degree (see Sect. 3.2), are important to plan experiments with the surface scattering apparatus. In particular the proper velocity selection of the ST and FT performed with the two disk velocity selector in Genova, has been possible following the detailed information obtained with the eight disks selector in the apparatus of Figure 4.

3 Experimental results and discussion

3.1 Anisotropy in the IR absorption: the J dependence of the alignment degree

Typical absorption signals A as a function of a molecular time-of-flight for $J = 1$ and $J = 2\,R$ transitions are given in Figure 6. Results are reported for both parallel and perpendicular laser polarizations and for a probed angular cone $\Delta\Omega \sim 10^{-5}$ str of the supersonic expansion. The same figure shows simulated values for the limiting case of C_2H_4 flying fully aligned ($M = 0$ for all J). A random orientation would provide $A_{\parallel} = A_{\perp}$. An aligned molecular beam provides an anisotropy in the absorption $\Delta A/A = 2(A_{\parallel} - A_{\perp})/(A_{\parallel} + A_{\perp})$. Qualitatively similar but significantly smaller effects have been measured in conditions of lower angular resolution (i.e. $\Delta\Omega \sim 10^{-4}$ str).

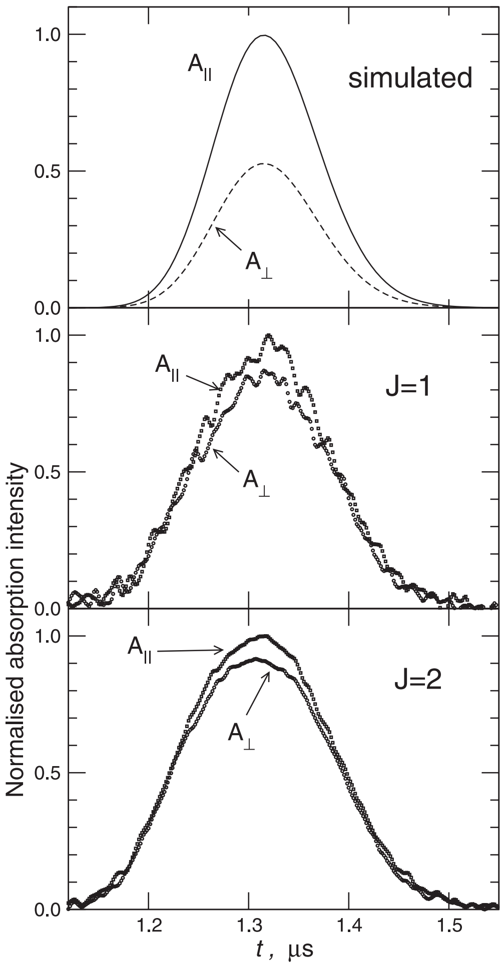

Fig. 6. Time of flight measurements for an ethylene supersonic beam seeded in He. For $J = 1$ the measured anisotropy effect $\Delta A/A = 0.07 \pm 0.03$ while for $J = 2$ $\Delta A/A = 0.05 \pm 0.01$. The upper panel shows the simulated maximum possible anisotropy effect in the absorption observable for a fully aligned beam.

The rotational lines intensity distribution reported in Figure 3 shows a nearly statistical behavior in the J distribution. A non thermal rotational distribution is possible for molecular beams where the collision rate does not permit complete thermalization, especially if relaxation channels with low probability per collision are present. The nuclear spin configuration exchange in systems containing hydrogen atoms is a typical example. The collisional molecular alignment process corresponds to a non statistical distribution of J projections along the beam axis and can be considered as a complementary aspect of the same phenomenon. Investigation on these aspects is going on. As previously noted more than 2/3 of the total population can be confidently assigned to $J \leq 2$ rotational states. This is an important information for developing simplified

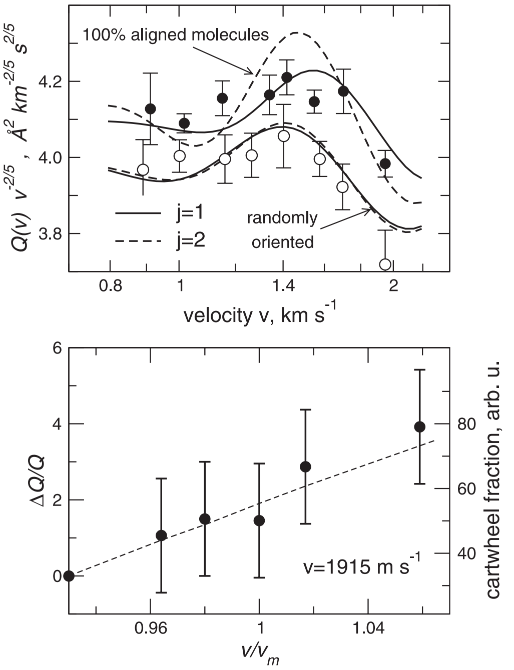

Fig. 7. Integral cross-sections for the scattering of ethylene by Ar targets. The angular resolution of the experiments is $\Delta\Omega \sim 10^{-6}$ str and the velocity resolution is 5% FWHM. Calculations and results in the upper panel are plotted as $Q \times v^{-2/5}$ as usual to emphasize the glory interference effect.

models able to describe the alignment process on the basis of observed quantities in the different experiments.

Even if present IR measurements are unable to resolve the velocity dependence of the molecular alignment, because of some uncertainty due to the convolution introduced by the optical multi-pass design (see Fig. 2), they provide quantitative information on the average alignment degree and on its J dependence. In addition they clearly show the importance to probe the supersonic molecular beam in narrow angular cones around its axis to enhance important features of the phenomenon.

3.2 Anisotropy in the gas phase scattering: the velocity dependence of the alignment degree

Figure 7 reports the integral cross-section Q for scattering of C_2H_4 molecules by Ar atoms. Experimental data, shown in the lower panel, have been obtained by locking the velocity selector on a typical molecular beam velocity ($v = 1915$ m s^{-1}) and varying the peak velocity v_m by a proper adjustment of the carrier gas composition. In this way an analysis of the cross-section variation $\Delta Q/Q$ along the molecular beam velocity distribution (i.e. versus the v/v_m ratio) has been possible. Such variations, since the collision energy is fixed, provide an information on the change of the alignment degree of the molecules as a function of their speed. More extensive measurements have also been performed [14] as a function of the collision velocity v, by selecting in this case for simplicity only three v/v_m values among the many reported in the lower panel of Figure 7. Specifically we have chosen the slow speed tail, $v/v_m = 0.93$ (which resemble the behaviour of the ST of the two disk velocity selector in Genova), the fast front $v/v_m = 1.07$ (which resembles the behaviour of the FT of the two disk velocity selector in Genova), and the central part $v/v_m = 1$ of the velocity distribution of several seeded beams. Some of the experimental data are shown in the upper panel of Figure 7 (for a more complete dataset refer to [14]).

For an analysis of $Q(v)$ and $\Delta Q/Q$ it is necessary to know to a high accuracy the interaction potential energy surface driving the scattering and also to adequately describe the collision dynamics. Several efforts and important progresses have been succeeded in this direction in the last years [2,7,10,15]. Simulations of $Q(v)$, for the two most populated rotational states $J = 1$ and 2 and for the two limiting cases of full and no molecular alignment are given in the upper panel of Figure 7. They show how the integral scattering cross-section at a given velocity increase as the alignment degree increases rather independently from the populated J state (i.e. Q being determined essentially by elastic events depends strongly on the M distribution but much less on the J distribution).

A simulation of $\Delta Q/Q$ as a function of v/v_M ratio at a fixed $v = 1915$ m s^{-1} including the populated J states and considering an increasing alignment degree, i.e. an increasing fraction of cartwheel like flying molecules, is shown in the lower panel of Figure 7. The comparison with measured $\Delta Q/Q$ values clearly indicate that, under the high angular and velocity resolution conditions typical of the apparatus of Figure 4, the molecular alignment degree (the fraction of cartwheel like molecules) increases with the molecular speed in a similar way as previously observed for diatomic molecules [1,2].

3.3 Anisotropy in the sticking coefficients: an application to surface scattering

The apparatus in Genova has been employed to investigate the effect of molecular alignment of the incoming ethylene molecules on the sticking probability S on Ag(001) [12]. The choice of this system is motivated by the relative weakness of the ethylene-silver bond (π-bonding) compared to the behavior of other transition metals where stronger (σ bonding) or dissociative chemisorption occurs. A weakly chemisorbed system is the most obvious candidate to observe possible effects of the initial molecular alignment on the sticking probability since, in presence of a deep chemisorption well, steering is expected to be more efficient in bending the molecular axis when it approaches the surface. Ag is pre-covered with O_2 since the latter species is known to promote ethylene adsorption in a very effective way, while keeping the adsorption energy close to the value proper of π bonding (about 0.4 eV/molecule). By selecting the slow (ST) or the fast (FT) tail of the supersonic distribution at the end of the expansion of a beam of ethylene seeded in He or Ne, we have been able to

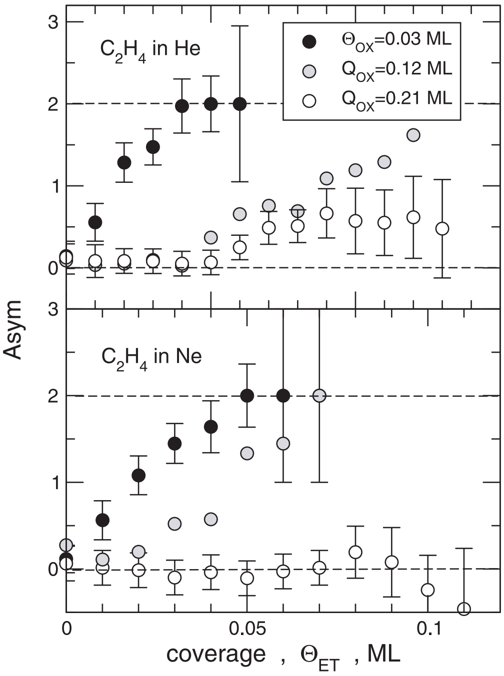

Fig. 8. Asymmetry in the sticking probability vs. ethylene coverage for different Θ_{OX}. Experiments with molecular beams seeded in Ne and in He, corresponding to a kinetic energy of 0.12 and 0.36 eV, are shown. For the sake of clarity, the error bars are shown only for the lowest and the highest Θ_{OX}. The dashed lines indicate the two limiting cases of minimum and maximum steric effect.

investigate directly the uptake of a supersonic beam consisting mostly of helicopters (ST) or mostly of cartwheels (FT). The energy difference between ST and FT is such that the change in S due to it, is comparable with the experimental error on S with the present beam flux.

In Figure 8 we report the sticking asymmetry

$$Asym = \frac{S_{ST} - S_{FT}}{0.5(S_{ST} + S_{FT})} \qquad (1)$$

as a function of the ethylene coverage, Θ_{ET}, for the uptake of ST and FT beams at different O$_2$ pre-coverages, Θ_{OX}. *Asym* is a quantitative estimate of the relative difference between the sticking probability for cartwheels and helicopters. We observe that: (a) in the low Θ_{ET} limit no asymmetry is present, independently of Θ_{OX}; (b) for Θ_{OX} up to 0.07 ML the asymmetry shows up immediately and increases with increasing Θ_{ET}; (c) in the high Θ_{OX} region, the asymmetry tends to appear only when Θ_{ET} exceeds some 0.05 ML. These results clearly demonstrate that: (a) the interaction between ethylene and bare or O$_2$ covered Ag sites is not affected by the hydrocarbon initial alignment; (b) a large steric asymmetry appears when interaction with pre-adsorbed ethylene molecules becomes relevant; (c) the balance between interaction with pre-adsorbed ethylene and with pre-adsorbed oxygen determines the coverage at which the asymmetry shows up, disclosing a more complex dynamics. We note that for the lower energy of incidence (the Ne seeded molecular beam) at given Θ_{OX} a smaller Θ_{ET} is needed to observe stereosensitivity. At high Θ_{OX} the steric effect tends to vanish. These phenomena are most probably connected with more efficient steering towards O$_2$ covered sites.

The steric asymmetry observed here is larger than the orientational anisotropy observed in the adsorption of polar molecules [16,17] and possibly even larger than the steric effects observed to date in the interaction in the gas phase. This is most probably due to the fact that sticking often requires relevant energy transfer to the surface which may be substantially affected by the alignment of the incoming molecule and by its interaction with bare and covered sites at the surface.

The effect of the rotational energy on the sticking coefficient has been recently observed for rotationally hot molecular beams of ethylene, and have been attributed to the large variation of the rotational energy [18], as induced by a substantial heating of the nozzle source. In the present case of cold supersonic beams, we have not probed the rotational distribution in the molecular beam as a function of the velocity of the molecules, so we cannot exclude some small change of the J population for ST with respect to FT. The large value observed for *Asym* can be explained only admitting a substantial change in the distribution of J between ST and FT coupled with a strong and non-monotonic dependence of the sticking probability for low J values. The latter hypothesis seems extremely unlikely considering the small energy separation between rotational levels for ethylene. As a further evidence, in a recent experiment [19] we have compared the FT of the beam obtained by the supersonic expansion of propylene seeded in He with the nozzle kept at room temperature with the ST of a similar beam but obtained with the nozzle at 358 K. Under such conditions molecules have exactly the same translational energy. We found that the ST for such a moderately hot nozzle behaves similarly to the ST of the beam obtained with the room temperature nozzle, thus further supporting our explanation in terms of different molecular alignment.

4 Conclusions

In the present joint investigation of the collisional cooling and alignment of C$_2$H$_4$ molecules in seeded supersonic beam important aspects of the collisional alignment process have been better characterized with respect to previous experiments with benzene [5,6]. Specifically the dependencies on velocity, rotational state and angular resolution have been more clearly defined. Moreover, an interesting application to the study of stereo-dynamics effect in surface adsorption processes have been performed. The obtained results represent important guidelines to carry out further joint experiments in order to have a better insight of the alignment process. In particular efforts will be addressed to characterize the angular and velocity dependencies of the phenomenon under increased angular resolution conditions. The rotational dependence analysis will be extended to higher J values. To complete the investigation of these effects, other molecules with different symmetry and mass will be analyzed. Hopefully, the obtained results will represent valuable information for the modeling of collisional alignment and to extend its applications to the investigation of stereodynamics effect both in gas phase and at surfaces.

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