What is Wrong with the Steric Asymmetry in Atom-Molecule Collisions?

A. Gijsbertsen[1], H. Linnartz[1], J. Kłos[2] and S. Stolte[1*]

[1]Laser Center and Department of Physical Chemistry, Vrije Universiteit Amsterdam, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands
[2]Institute of Theoretical Chemistry, University of Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands

Abstract

The sign of the steric asymmetry S in rotationally inelastic state resolved atom-molecule collisions is questioned. Both experimental and theoretical results for collisions of Ar or He with NO (or ON) and Ar with OH (or HO) are discussed. Studies involve quantum state-selected crossed molecular beam experiments. In the case of NO, a striking oscillatory behavior of S as function of the rotational state after collision is observed. Full quantum mechanical scattering calculations with HIBRIDON reproduce the oscillation as far as the absolute value of S is concerned, but no consistency is obtained for the sign. On the other hand, comparable theoretical results for OH agree with experimental results for both absolute value and sign of S. The inconsistencies between experiment and the different theoretical approaches are described and possible solutions are discussed.

1. Introduction

In everyday life collisionally induced processes are non-directional. Specific orientations seem not to play a role as all orientations are present in a sample. However, one expects that nature will have directional preferences. For example, the collisional behavior of an NO molecule is expected to be somewhat different when the N-end or the O-end is hit. These orientational dependencies are important to unravel the dynamics of inelastic and reactive collisions. Nowadays, directional dependencies can be studied up to the level of individual quantum states using state of the art experimental and theoretical techniques. Careful initial molecular state preparation, using sophisticated molecular beam techniques allows experiments with quantum state controlled molecules and high resolution spectroscopic probes make it possible to study reaction products state-specifically.

Orientation effects in collisions of a diatomic molecule with a rare gas are described using the steric asymmetry ratio that is defined as

$$S = \frac{\sigma^{Head} - \sigma^{Tail}}{\sigma^{Head} + \sigma^{Tail}} \tag{1}$$

where σ^{Head} and σ^{Tail} denote the integral collision cross sections for molecules oriented preferentially with their head or tail towards the incoming atom. This means that when S is positive, head collisions contribute more to a specific final rotational state than tail collisions and vice versa. The steric asymmetry ratio indicates the anisotropy of the interaction potential and is an effective observable as most instrumental errors cancel each other in nominator and denominator.

In recent work [1], a mathematical discussion is given on the sign of the steric asymmetry in previous work on inelastic collisions with oriented molecules. This work was done mainly on NO [2–4] and OH [5]. Ref. [1] made clear that inconsistencies

exist on the sign of S between theory and experiment. This may have a number of reasons varying from a wrong definition to a fundamental physical problem.

In this comment, first a typical state-selective collision experiment is described to elucidate the discussion on the sign of S. A historical overview is given to summarize conclusions obtained so far and to emphasize the existing discrepancies. Finally, speculations on the reason of the emerged disagreement between theory and experiment are given.

2. Experimental details

To render a better insight into the experimental methods, collisions of a rare gas with NO will serve as an example in this section. The experiments with OH are similar. The experimental setup is a crossed beam machine as shown in Fig. 1 [3]. With a repetition rate of 10 Hz two pulsed valves – the NO beam valve with 16% NO in Ar and the rare gas beam valve – are used to adiabatically expand gas pulses into a vacuum chamber, resulting in low final rotational temperatures. The cooled NO molecules are disposed mostly in the lowest rotational level of the electronic $^2\Pi$ ground state with total angular momentum quantum number $j = \frac{1}{2}$.

In the case of NO, rotational levels carry a minute (parity) splitting, the so-called λ-doublet. The symmetry index $\epsilon = -1$ or 1 distinguishes between the two equally populated components of the λ-doublet (with respectively "f" and "e" labels). The molecules in the low field seeking (f) upper component of the λ doublet with symmetry index $\epsilon = -1$ are focussed into the collision region using a 2 m long hexapole. Molecules in the high field seeking (e) lower component ($\epsilon = 1$) of the λ doublet are pulled away from the center of the hexapole. This means that it is possible to prepare a molecular beam of molecules that are all in one single quantum state $j = \frac{1}{2}$, $\overline{\Omega} = \frac{1}{2}$, $\epsilon = -1$. $\overline{\Omega}$ denotes the (absolute value of the) projection of the total angular momentum on the molecular axis. $\overline{\Omega}$ can take values $\frac{1}{2}$ and $\frac{3}{2}$ as only the electron spin and orbit angular momenta have a non-zero projection on the molecular axis.

As a next step the hexapole focussed NO molecules (in the collision region) are oriented in an essentially homogeneous 13.5 kV/cm field, produced in between two pairs of rods that are placed perpendicular to the relative velocity v_{rel} (see Figs. 1 and 2). A negative voltage is applied onto the pair of He-rods (rare gas rods) or onto the pair of NO-rods to produce the orientation field, while the other pair of rods is at ground. The pairs of rods are labelled after the incoming particles that pass them first (Fig. 2). As the NO molecules are in a low field seeking state, they will orient with their negative ends towards the negative rods. Assuming that the NO dipole moment is such that N^-O^+ [7–11], application of the negative voltage onto the NO-rods yields O-end collisions

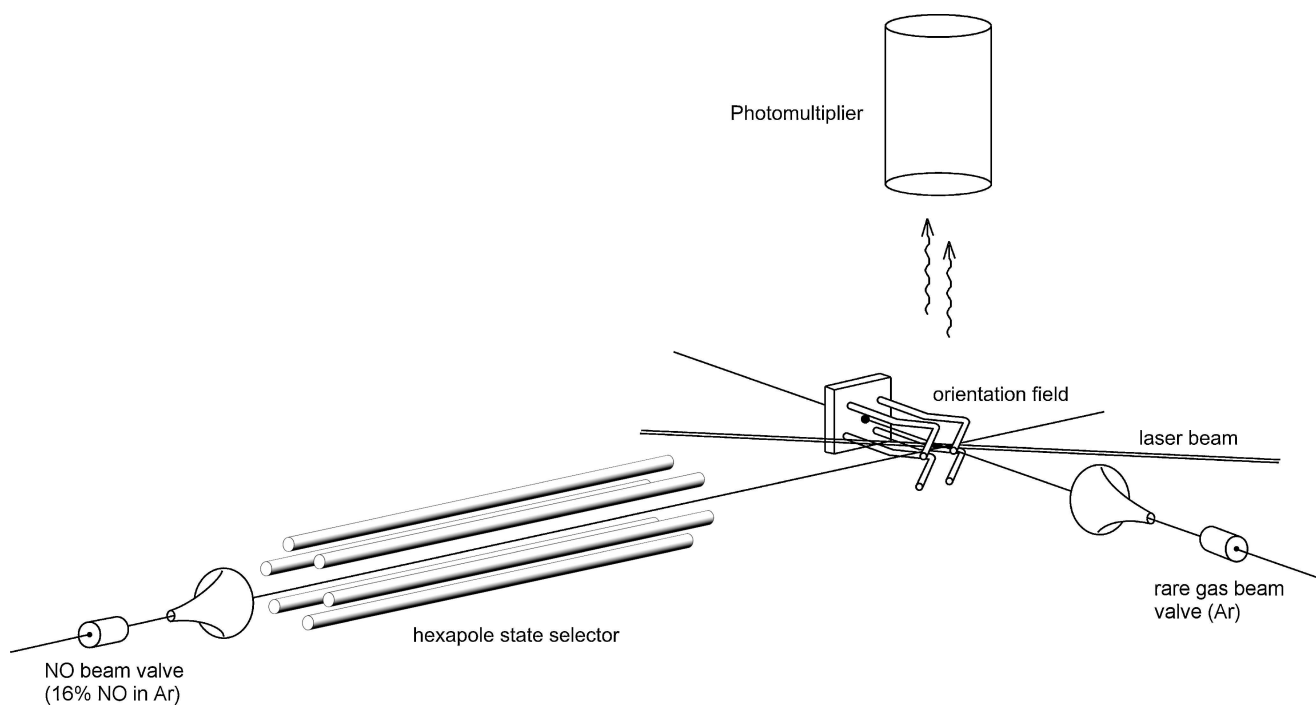*Author to whom correspondence should be addressed; e-mail: stolte@few.vu.nl

Fig. 1. Experimental setup for Ar-NO collisions [3]. (Reprinted from Chem. Phys. Lett. 313, de Lange *et al*, Steric asymmetry in state resolved NO-Ar collisions pp. 491–498. Copyright (1999) with permission of Elsevier)

whereas switching the negative voltage onto the He rods yields N-end collisions (Fig. 2).

Due to a collision with an Ar or a He atom, the oriented NO molecule can be excited to a higher rotational state (j', $\overline{\Omega}'$, ϵ'). The amount of molecules (giving the cross section σ) that is scattered into a certain (j', $\overline{\Omega}'$, ϵ') state is detected by Laser Induced Fluorescence (LIF) via the electronically excited $A\Sigma^+$ state of NO. With the cross section for both N-end and O-end (head and tail) collisions measured, the steric asymmetry S is obtained following Eq. (1).

Experiments on collisions of Ar with NO [3, 12] were performed on the same experimental setup as those on collisions of
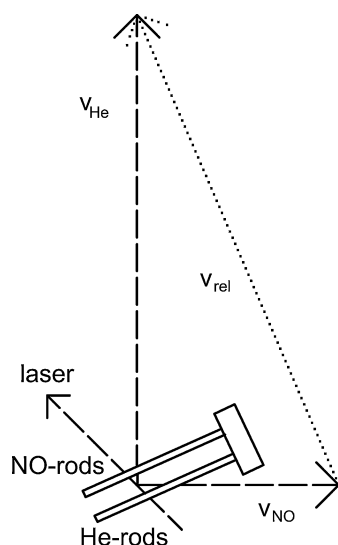
He with NO [13]. The replacement of Ar ($v_{Ar} = 560\,\text{m/s}$) in the rare gas beam by He ($v_{He} = 1760\,\text{m/s}$) alters the direction of the relative velocity and the alignment of the orientation field has to be adapted. The orientation field lines have to be parallel to the relative velocity. Work on collisions between Ar and OH was performed by ter Meulen and coworkers, a discharge ring was used to produce the OH radicals and a double hexapole was used for focussing [5].

3. Historic overview

First experimental evidence for large orientation effects in rotationally inelastic Ar-NO (ON) collisions, was obtained by Van Leuken *et al.* [2]. In their convention, the N-end and the O-end of the NO molecule were defined as head and tail, respectively. They discovered that for Ar-NO, S exhibits a striking undulatory character at a collision energy of $E_{tr} = 475\,\text{cm}^{-1}$. Later on these experimental studies were extended [3, 6, 12]. The $\Delta j = j' - j$ dependence of the steric asymmetry for Ar-NO collisions at $E_{tr} = 475\,\text{cm}^{-1}$ and for He-NO collisions at $E_{tr} = 509\,\text{cm}^{-1}$ is shown in Fig. 3 (upper and center panel, respectively). When the orientation field is applied such that the N-end of the NO molecule is favored to point towards the incoming rare gas atom, the collision yields mostly $\Delta j = even$ transitions. For O-end collisions, $\Delta j = odd$ transitions are found to be preferred.

The strong oscillation of S cannot be understood using only classical mechanics. Ar-NO and He-NO Potential Energy Surfaces (PESs) [14–16] show an egg-alike shape in which the N-end extends further from the center-of-mass than the O-end. When one assumes Ar-NO collisions to be collisions between an egg shaped hard shell (NO) and a hard sphere (Ar), there is no way to explain the effect that N-end collisions yield mostly $\Delta j = even$, while O-end collisions yield mostly $\Delta j = odd$. The amount of torque that can be applied is limited by the collision energy and the lever. This lever is the distance between a line perpendicular
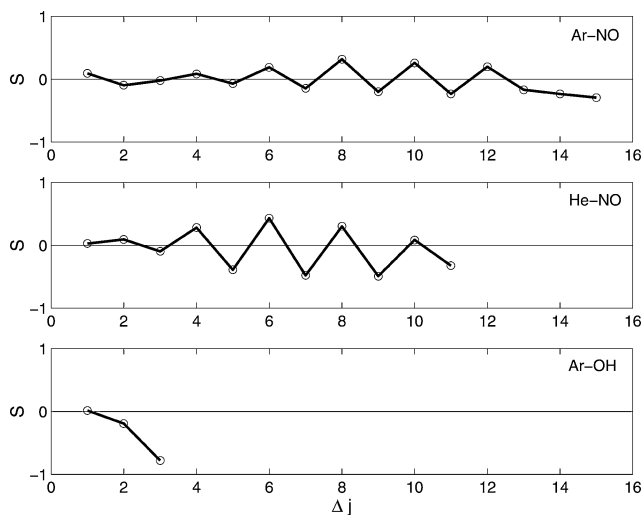

Fig. 2. Orientation geometry. The pairs of rods are labelled after the incoming particles that pass them first. The orientation field is produced by applying a voltage on the pair of NO-rods or on the pair of He-rods, see also Fig. 1. The other pair remains grounded. It should be noted that $v_{NO} = 590\,\text{m/s}$ and that $v_{He} = 1760\,\text{m/s}$.

Fig. 3. Experimental steric asymmetry ($\epsilon = \epsilon' = -1$) as a function of $\Delta j = j' - j$ for spin orbit conserving collisions of: Ar with NO (upper panel) at a collision energy of $E_{tr} = 475\,\mathrm{cm}^{-1}$ [12], He with NO (center panel) at a collision energy of $E_{tr} = 509\,\mathrm{cm}^{-1}$ [12, 13] and Ar with OH (bottom panel) at a collision energy of $E_{tr} = 746\,\mathrm{cm}^{-1}$ [17]. It should be noted that for experiments on NO the N-end is regarded as the head of the molecule, while for collisions of Ar with OH the O-end is regarded as head of the molecule. Earlier data for Ar-NO [3] have been improved using a flux to density transformation that transformed LIF intensities into proper state-to-state cross sections. This treatment enhanced the amplitude of S, but not its sign. The oscillation of S for collisions of NO with He shows the same sign but a larger amplitude.

to the shell (along which the force acts) and the center of mass. The (linear) momentum parallel to the hard shell is conserved, while that perpendicular to the shell is transformed into rotation, i.e. from a classical point of view one would expect that the end of the molecule where the largest torque can be applied (the N-end) is preferred for producing rapidly rotating molecules (large Δj). Molecules that after collision are in low rotational states (small Δj) are expected to be due mostly to collisions onto the end of the molecule where the maximally applied torque is smaller (O-end), i.e. no alternation (of S) is expected from this model; classical mechanics cannot describe the observations.

Moreover, for excitations to the highest allowed rotational states the oscillation decreases and a negative value for S (indicating O-end preference) has been observed for large Δj [2–4, 12]. At that time, the sign of the experimental value of S was in agreement with the theoretical prediction of Refs. [2–4, 12]. Recently the experimental setup was improved to allow for more sensitive experiments and the latest experimental data by De Lange *et al.* also showed nice agreement with theory [3].

For collisions of Ar with OH, the oscillatory behavior of S as function of j' turned out to be absent [5] (see also Fig. 3, lower panel). O-end collisions mostly result in low rotational states while H-end collisions mostly yield high rotational states. Full quantum mechanical theoretical results correspond reasonably well to the experimental results. Van Beek *et al.* [5] defined the (negative) O-end of the molecule as being the head and the (positive) H-end as being the tail of the molecule (Eq. (1)). This definition is opposite to what implicitly follows from the potential energy surfaces [18] that were used for close coupling calculations. In these PESs, $\theta = 0$ corresponds with an H-end (Tail) collision. For all NO PESs $\theta = 0$ corresponds with an N-end (Head) collision [13–16]. When using these PESs in calculations,

one should be well aware of and very careful with the orientation of the PESs.

Up to this point, theory and experiment seemed to correspond very well. Some recent results, however, raised some doubt concerning the sign of S. In the next section reasons to question the sign of S are given.

4. Reasons to doubt the sign of S

The first inducement to question the correctness of the sign of the steric asymmetry from previous measurements, were some results obtained with a new quasi quantum mechanical model [19]. These model calculations were performed to shed more light on the nature of the oscillations of S. Quantum mechanics alone does not provide physical insight in the reason of the steric effect. Results for He-NO and Ar-NO corresponded remarkably well to the experimental ones, only the sign turned out to be wrong. Calculations with the quasi quantum mechanical model on Ar-OH, however, reproduced the experimental sign of S [19].

Searching for reasons of the "erroneous" model calculations, it was noted that results for collisions with NO are opposite to that what is expected from a simple classical "ball-and-stick" model. When taking a close look at the upper panel of Fig. 3, one sees that for high rotational states S becomes negative. This implies that these high rotational states are mostly produced by collisions onto the O-end of the NO molecule. Looking at the Ar-NO PESs [14, 15] one would expect something different. For transitions to high rotational states, the repulsive part of the potential dominates. In the Ar-NO PESs introduced by Alexander [14, 15] one can immediately see that the N-end extends further from the center-of-mass. From a (classical) point of view one would expect the N-end to be preferred, as the torque that can be applied to the N-end is larger. When a stick is attached to a ball, it is easier to make the system rotate by hitting the stick, than by hitting the ball, i.e. from this simple classical ball-and-stick model an S is expected with a sign opposite to the sign resulting from the measurements.

For collisions of the less homo-nuclear OH molecule with Ar this becomes even more clear and indeed the ball-and-stick model corresponds to the measurements. The H-end (stick) is preferred for high rotational states in both experiment and theory [5]. The experimental steric asymmetry for the Ar-OH system is plotted in the lower panel of Fig. 3. Recent full quantum mechanical (HIBRIDON) [1, 20] Ar-OH calculations, resulted in a sign opposite to the sign of previous results for S. Identical calculations on He-NO, however, yielded a sign of S that was similar to the experimental sign. The orientation of the potential energy surfaces was checked and did not account for this disagreement. Close inspection of the HIBRIDON source code showed that the prepared wave function carried an orientation that is opposite to the one assumed [2, 4]. This offers an explanation for the disagreement of the recent theoretical sign of S for Ar-OH with previous results and with the ball-and-stick model. However, when the theoretical sign of S for collisions of Ar with OH flips, it should also flip for Ar-NO and He-NO, i.e. there is still a disagreement between the experimental and theoretical sign of S for collisions with NO.

The fact that the Ar-OH PESs [18] were specified oppositely to the definition of S [5] (H-end as head instead of O-end) might be the reason that the disagreement between theory and experiment (due to an error in HIBRIDON) for Ar-OH was not found before. Very recently, some new close coupling scattering calculations have been performed on He-NO [21].

These calculations, that were unrelated to previous HIBRIDON calculations, also yielded a sign for S opposite to the experimental result for He-NO.

To summarize, a flip of the theoretical sign of S for collisions with NO, while keeping the sign for collisions with OH as it was reported before, makes all theoretical results in agreement with the ball-and-stick model. There remains, however, a sign difference between the theoretical and the experimental results for collisions with NO. At this point, the logical conclusion is that something is wrong with the experimental sign of S for the NO experiments.

Although tested before, it was decided to test the experimental sign of S once more. The oscillation for S is largest for the He-NO system that for this reason has been used. To orient the molecules during the experiment, a negative voltage was applied that can be switched onto the He or onto the NO-rods (see also Fig. 2). The absolute value of the small electric dipole of NO ($v = 0$, $X^2\Pi$) has been measured with high precision ($0.1574 \pm 0.014\,\mathrm{D}$) by Hoy *et al.* [22] and their result is in reasonable agreement with the *ab initio* value ($0.1732\,\mathrm{D}$) [7]. All charge distributions calculated using *ab initio* methods correspond to N^-O^+. To our knowledge, the sign of the NO dipole moment has not been determined experimentally so far. The NO molecules are all in the low field seeking state that is selected by the hexapole. Orientation should be such that the N-end points towards the the rods to which the negative voltage is applied.

First the orientation field was taken out of the machine to measure the voltages on the rods. When the input of the HV-switch was 0, a negative voltage was measured on the He rods; when the input was 1, a negative voltage was observed on the NO-rods. This gives N-end and O-end collisions, respectively, as molecules in a low field seeking state orient with their positive end towards the positive electrode. The orientation field was placed back in the setup and LIF measurements were performed. Background subtracted signals were collected for $j' = 4.5, \Omega' = 0.5, \epsilon' = -1$ in the R_{21} branch (for both HV-switch inputs): when the HV-input was 0 (N-end collisions) a signal of $67\,\mathrm{mV}$ was recorded, when the HV input was 1 (O-end collisions), $29\,\mathrm{mV}$ was observed. For the steric asymmetry for $j = 4.5$ this gives: $S = (67 - 29)/(67 + 29) = +0.40$ which means N-end preference as measured before (see also Fig. 3). The experimental error on S is estimated to be ± 0.15. As a consequence the discrepancy continues to exist and the question remains what the origin of the disagreement is. No answer to this question has yet been found. In the next section some speculations are given.

5. Concluding remarks

The current status is that "revised" *quantum mechanical calculations* (HIBRIDON) yield results that are consonant with the ball-and-stick model for the Ar-OH, Ar-NO and He-NO systems. Consonant with the ball-and-stick model means that high rotational states are preferentially the result of collisions on the end of the molecule at which the largest torque can be applied (the N-end for NO and the H-end for OH). *Experimental results* for the Ar-OH system correspond to the revised HIBRIDON calculations and to the ball-and-stick model. For collisions of NO with Ar and He, *experimental results* oppose the ball-and-stick model and consequently the sign of the (experimentally obtained) steric asymmetry S opposes the "revised" quantum mechanical results.

An error in the experimental procedure for experiments with NO, introducing an erroneous sign, would solve all disagreements between theory and experiment. Some simple tests, however, appear to rule out such errors.

Another possibility to account for the sign difference for NO is an error in the He-NO and the Ar-NO PESs. This is very unlikely: there is good quantitative agreement between the absolute value of S in (Ar-NO and He-NO) experiment and theory [3, 13]. The possibility that the CEPA and CCSD(T) PESs are not accurate enough, can be excluded. This does not exclude that the labels for the N-end and the O-end in the PESs can be wrong. It is, however, very unlikely to assume that the heavier O-end extends further from the center-of-mass than the N-end. Quasi-quantum mechanical calculations and full quantum mechanical calculations that are independent of the HIBRIDON code support the finding that the simple classical ball-and-stick model can be applied.

For calculation of the experimental steric asymmetry, the head (N-end) of the NO molecule is assumed to be negative while the tail (O-end) should be positive. However, the actually *observed* steric asymmetry S is given by:

$$S = \frac{\sigma^- - \sigma^+}{\sigma^- + \sigma^+}. \tag{2}$$

The cross sections σ^- and σ^+ indicate the cases in which the negative and the positive end of the molecule preferentially point towards the incoming atom. In terms of Eq. (1) the negative (positive) end of the molecule is defined as its head (tail). When the sign of the NO ($v = 0$, $X^2\Pi$) dipole moment would be reversed – N^+O^- instead of N^-O^+ – the experimental sign of S would be in agreement with the ball-and-stick model. Although the absolute value of the NO dipole moment is well known, even the highest precision experiments could not determine the sign of the NO dipole moment unambiguously, i.e. N^-O^+ or N^+O^- [23]. The sign of the dipole moment has not been measured, but it has been calculated. Large series of *ab initio* calculations reported N^-O^+ [7–11]. Taking into account indirect evidence from recent experiments by Matsiev and coworkers [24] and predictions by Drabbels and Wodtke [23], a flip of the sign of the dipole moment seems to be not that feasible.

The origin of the sign difference between the theoretically and experimentally obtained values of S remains unclear for the moment. Some new experiments might shed light on this subject. Collision experiments can be repeated with rare isotopes of NO, to get an answer on the shape of the NO shell. In the case of $^{14}N^{18}O$, the center-of-mass is shifted towards the O-end of the molecule. It is expected that the N-end then is even more preferred for high rotational states and it will be interesting to see whether stronger effects are observed. Another approach would be to verify experimentally the sign of the dipole moment of NO. This might be achieved in an experiment in which the molecules are first oriented and subsequently dissociated using femto-second laser pulses. Nevertheless, the situation is such that considerable progress has been obtained in the last years and that at least consistent definitions are used now. New experiments are necessary to unravel the remaining question: what is wrong with the steric asymmetry in NO-rare gas collisions?

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