

Molecular Reorientation in Collisions of OH + Ar

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(Received 4 October 2000)

Oriental effects in rotationally elastic collisions of OH with Ar were studied in a crossed molecular beam setup. A static electric field was applied to orient the molecules before the collision. After the collision the orientation was measured by using a narrow-band laser system to probe the Stark-split states corresponding to different orientations. Differential and integral cross sections for reorientation of the molecular axis have been determined as a function of the initial orientation. The cross section for reorientation by one quantum is 25 \AA^2 with a preference for O-end collisions.

DOI: 10.1103/PhysRevLett.86.4001

PACS numbers: 34.50.Ez, 33.15.Bh, 34.50.Lf, 82.20.Rp

Molecular collision studies have delivered valuable information about the intermolecular forces that govern the properties of matter. Thus far the most detailed information is obtained from the study of single collisions in crossed beam experiments where parameters such as the relative velocity and the internal states of the collision partners are varied [1]. Still the obtained results reflect only the average of the intermolecular potential over the relative orientations of the collision partners. The relative orientation is, however, a key factor in determining the outcome of the collision. Whereas a specific orientation may lead to a chemical reaction the same reaction may be prohibited when the molecules are oriented in the opposite direction. Collision experiments are generally performed with nonoriented molecules and steric effects of the intermolecular forces stay concealed.

Control and detection of the relative orientation is, however, complicated. The relative orientation of the collision partners before a collision can be prepared using static electric fields [2] and laser techniques [3], and the *orientation of angular momentum* after the collision can be determined for reactive [4] and nonreactive collisions [5,6]. In the absence of external fields, however, angular momentum orientation corresponds to alignment (rather than orientation) of the molecular axis.

In this experiment we use molecular beams and an electrostatic state selector to prepare the initial quantum states. An electric field is applied to orient the molecules before the collisions. With a narrow-band laser system we are able to measure, by virtue of the Stark splitting, the final quantum state and the *orientation of the molecular axis* after the collision and to determine the differential cross section. To our knowledge no experiments have been reported thus far on collision-induced molecular reorientation. The methods described in this Letter can be used in a wider range of molecular dynamics studies such as photodissociation and chemical reaction experiments. The high state resolution allows for an unprecedented detailed comparison with theory without averaging over many quantum states and orientations. This is particularly interesting for collisions of open-shell molecules, since the multiple potential sur-

faces which govern these collisions give rise to quantum interference effects which, in general, are washed out if the results are averaged.

The OH-Ar system has become a benchmark system to study the interactions of open-shell molecules. Two *ab initio* potential energy surfaces have been developed [7] which have been compared with spectroscopic studies on the van der Waals complex [8] and inelastic collision experiments [9]. In this Letter we report on reorientation of the molecular axis in rotationally elastic collisions ($\Delta J = 0$) of OH($X^2\Pi_{3/2}, v = 0, J = \frac{3}{2}$) with Ar.

In our pulsed, crossed molecular beam experiment [9,10] (Fig. 1) the OH beam is produced by a pulsed dc discharge in H₂O seeded in Ar at the orifice of the valve. After the cooling due to the expansion, the OH radicals enter an electrostatic state selector which focuses OH molecules in a specific state in the collision zone where the OH and Ar beams cross at right angles. The OH radicals are oriented by a static electric field which is parallel to the relative velocity of the collision partners. This field is produced by four parallel rods which are set pairwise at a positive or negative high voltage. By changing the polarity of the rods, the OH radicals can be oriented with the H or O end towards the Ar atoms. The degree of orientation is $\langle \cos\theta \rangle = 0.575$ for molecules with $|M_J| = \frac{3}{2}$ and $\langle \cos\theta \rangle = 0.165$ if $|M_J| = \frac{1}{2}$, which is close to the quantum mechanical limit of 0.6 and 0.2, respectively. In this experiment molecules in the $M_J\Omega = -\frac{9}{4}$ state are selected by the state selector. Here,

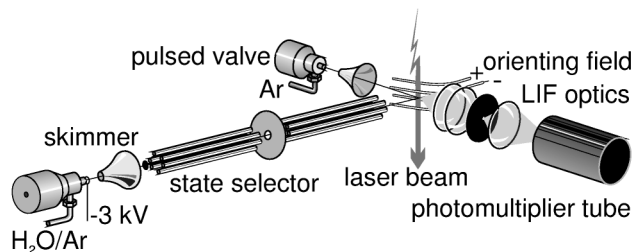


FIG. 1. Schematic representation of the experimental setup.

TABLE I. OH beam characteristics and collision signals. The expectation value of the angle between the electric field and the OH internuclear axis is given by $\langle \cos\theta \rangle$; a positive or negative value indicates that the OH molecule is directed with the H end or O end in the direction of the electric field vector, respectively. FL represents the fractional loss of population of the initial state. The relative cross section σ , the steric asymmetry factor S , and the scattering angle θ_{FWHM} have been defined in the text.

State			Beam			Outscattering		Inscattering		
ϵ	$ M_J $	$M_J\Omega$	$\langle \cos\theta \rangle$	Population	Width (GHz)	FL(%)	S(%)	σ (arb. units)	$S(\%)$	$\theta_{\text{FWHM}}(^{\circ})$
f	$\frac{3}{2}$	$-\frac{9}{4}$	-0.575	86.0 ± 0.3	0.26 ± 0.01	26.6 ± 0.7	0 ± 6	11.5 ± 1.1	-2 ± 14	7 ± 1
f	$\frac{1}{2}$	$-\frac{3}{4}$	-0.165	12.5 ± 0.1	0.17 ± 0.01	25.6 ± 0.2	7 ± 4	3.3 ± 0.5	15 ± 5	12 ± 1
e	$\frac{1}{2}$	$+\frac{3}{4}$	+0.165	1.3 ± 0.3	0.61 ± 0.15	1.2 ± 0.5	13 ± 6	17 ± 3
e	$\frac{3}{2}$	$+\frac{9}{4}$	+0.575	0.2 ± 0.1	0.50 ± 0.07	1.0 ± 0.3	-6 ± 1	25 ± 7

the notation $M_J\Omega$ is used to refer to the Λ doublet and $|M_J|$ substates which correspond to different orientations with respect to the electric field (Table I). The collision energy is $750 \pm 160 \text{ cm}^{-1}$ [9].

After the collision the OH molecules are detected in the collision zone by laser-induced fluorescence (LIF) using the $A \leftarrow X$ transition around 308 nm. In zero electric field the lower Λ -doublet state (e) can be probed only by a P or R transition, while the upper state (f) can be detected only using a Q or S transition [11]. In the presence of the orienting electric field the Λ -doublet states are Stark mixed and split. The Stark splitting allows us to resolve the $M_J\Omega$ states corresponding to different orientations. The parity mixing results in additional spectroscopic transitions, indicated by a prime, which go to the same $A^2\Sigma$ state as the zero-field transitions, but start from the other Λ -doublet component. Only the strongest transitions have been used: $P_1(1) + P_1(1)'$ and $Q_1(1) + Q_1(1)'$. To resolve both Λ -doublet components and the Stark-split M_J states a narrow-band laser system was used.

The P spectrum of the unperturbed OH beam is depicted in Fig. 2. From the Stark splitting of 2.451 GHz between the $-\frac{9}{4}$ and the $-\frac{3}{4}$ lines the strength of the orienting electric field ($|\mathbf{E}_{\text{orient}}| = 7.92 \pm 0.05 \text{ kV/cm}$), the positions of the $+\frac{3}{4}$ and the $+\frac{9}{4}$ lines, and degree of orientation (Table I) were calculated. In the analysis of the beam and collision-induced spectra, the central line positions were fixed at the measured ($-\frac{9}{4}$ and $-\frac{3}{4}$ states) and calculated frequencies ($+\frac{9}{4}$ and $+\frac{3}{4}$ states). The spectra could be analyzed by assuming a Gaussian profile with a full width at half maximum (FWHM) of 0.16 GHz. This width is the result of the laser bandwidth of 0.10 GHz, the hyperfine splitting in the ground state, and the power broadening due to saturation. The hyperfine splitting of the $A^2\Sigma$ state could easily be resolved, resulting in two lines for each Stark-split state. Since the laser power is high enough to saturate all transitions, the relative areas below the line profile are equally proportional to the relative population.

Initially most molecules (86%) are in the $-\frac{9}{4}$ state, some molecules (12%) are in the $-\frac{3}{4}$ state, and the population of the e states is negligible. The Doppler width of the

lines varies quite significantly. The width is largest for the $+\frac{3}{4}$ and the $+\frac{9}{4}$ states which are blocked by the state selector, and can only reach the collision area by secondary collisions within the setup. The difference in width for the $-\frac{3}{4}$ and $-\frac{9}{4}$ states is caused by the focusing properties of the state selector. A simulation of the trajectories in the state selector leads to a Doppler width of 0.078 and 0.205 GHz for the $-\frac{3}{4}$ and $-\frac{9}{4}$ states, respectively. A convolution with the total bandwidth of 0.16 GHz gives a linewidth of 0.18 and 0.26 GHz, respectively, in agreement with the observed widths.

The collision data were collected by scanning the laser frequency around the P and Q transitions. Both spectra were recorded 10 times with the O end and 10 times with the H end directed towards the Ar atom. Each spectrum consists of 4000 single shot points, which were collected alternately with and without Ar collisions. Subtraction of the points recorded without collisions from those with collisions yields the collision-induced spectrum (Fig. 2).

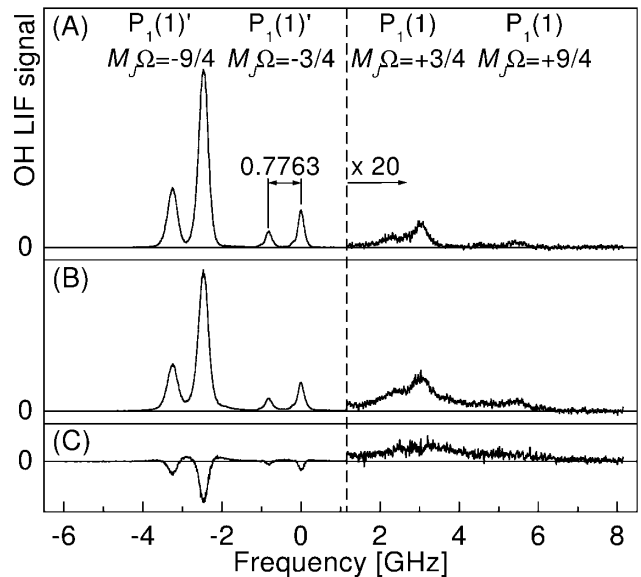


FIG. 2. OH saturated LIF spectra of the $P_1(1) + P_1(1)'$ transition: (a) without collisions; (b) with collisions; (c) collision-induced spectrum (with collisions - without collisions).

The collision-induced spectra contain two contributions: one “negative” spectrum with narrow lines due to the decrease of molecules in the beam and one “positive” spectrum with Doppler broadened lines representing the scattered molecules (Fig. 3). The negative spectrum necessarily has the same parameters (position and width) as the unperturbed beam spectrum. Since the direction of the laser beam is perpendicular to the scattering plane, the Doppler profile of the scattered molecules is symmetric around the center of the beam. We assume that the signal of the scattered molecules can be represented by a Gaussian line profile. This is a good approximation when the molecules are scattered in the forward or backward direction, but not when the molecules are scattered sideways. Nevertheless, we believe that the scattered molecules can be analyzed with a Gaussian distribution for the following reasons. First, for $\Delta J = 0$ transitions the differential cross section is expected to be peaked in the forward direction [12]. Second, the $+\frac{3}{4}$ and the $+\frac{9}{4}$ peaks consist only of a positive line, which can be well fitted to a Gaussian profile. Last, when fitting a positive contribution to the $-\frac{9}{4}$ and the $-\frac{3}{4}$ peaks, the resulting lines have a width of 0.7 and 1.2 GHz, respectively, which corresponds to an average scattering angle θ of 7° and 12° , respectively. This indicates that the molecules are indeed forward scattered. The P and Q spectrum are analyzed independently, but

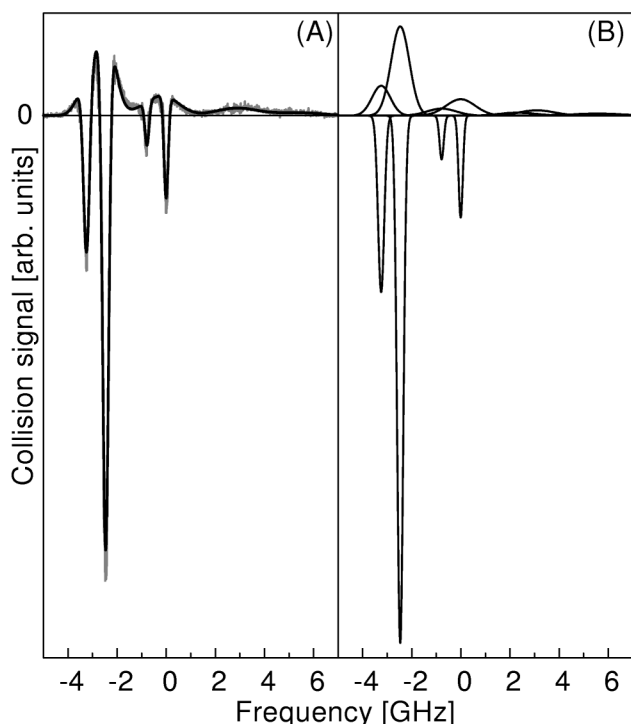


FIG. 3. OH collision-induced spectra of the $P_1(1) + P_1(1)'$ transition: (a) measured spectrum identical to Fig. 2c (gray dots) and the resultant of all fitted lines (solid line); (b) fit for separate signals; negative lines represent a decrease of the initial beam signal; positive lines represent the Doppler distribution of the scattered molecules.

they contain the same information. The averaged results of the P and Q spectra are presented in Table I. The reproducibility of our experiments indicates a precision of 2% to 5%. However, we have determined in previous work with this apparatus that systematic errors of 10% in calibration are present, due to, for example, incomplete saturation of the LIF transitions in the wings of the laser beam. The error ranges given in Table I are a combination of these statistical and systematic uncertainties.

Two parameters are extracted from the collision-induced spectra. The first is the cross section for reorientation with respect to the electric field averaged over collisions at the H and O ends of the molecule

$$\sigma_{M_J\Omega \rightarrow M_J'\Omega'} \equiv \frac{1}{2} [\sigma_{\text{HO-Ar}} + \sigma_{\text{OH-Ar}}],$$

and the second is the steric asymmetry of this cross section, which describes the effect of the initial OH orientation with respect to the Ar atom

$$S_{M_J\Omega \rightarrow M_J'\Omega'} \equiv \frac{\sigma_{\text{HO-Ar}} - \sigma_{\text{OH-Ar}}}{\sigma_{\text{HO-Ar}} + \sigma_{\text{OH-Ar}}} \times 100\%.$$

Here $\sigma_{\text{HO-Ar}}$ and $\sigma_{\text{OH-Ar}}$ represent the cross section for the $M_J\Omega \rightarrow M_J'\Omega'$ transition when the OH radical is initially directed towards the Ar atom with the O end or the H end, respectively.

A collision-induced P spectrum is depicted in Fig. 3 and the results obtained from the analysis of the collision spectra are presented in Table I. The total (elastic + inelastic) cross sections for scattering out of the $M_J\Omega$ states are proportional to the fractional population loss (FL) of these states, which is obtained by dividing the collision-induced population decrease of a state by the initial population of this state. The fractional losses for the $-\frac{9}{4}$ and $-\frac{3}{4}$ states were found to be nearly equal within the experimental accuracy: $\text{FL}_{-9/4}/\text{FL}_{-3/4} = 1.04 \pm 0.04$. This is consistent with results obtained by Hain *et al.* on OD + Ar, for which they found equal cross sections within their detection limit [6].

The relative cross sections σ are given by the area of the positive peaks in Fig. 3b. Since 14% of the population is distributed over states other than the $-\frac{9}{4}$ state, the measured cross sections are actually a sum over state-to-state cross sections, dominated by the $\sigma_{-9/4 \rightarrow M_J'\Omega'}$ cross section. The largest signal increases are found for the states with the highest initial population. This indicates that the elastic cross sections [$\Delta J = 0, \Delta(M_J\Omega) = 0$] are much larger than the reorientation cross sections [$\Delta J = 0, \Delta(M_J\Omega) \neq 0$]. To obtain an estimate of the relative reorientation cross sections we use a simple model. Assuming that all collision-induced transitions with equal reorientation (same $|\Delta M_J\Omega|$) have equal cross sections, our results are reproduced if $\sigma_0:\sigma_{6/4}:\sigma_{12/4}:\sigma_{18/4} = 100:15:7:8$, where σ_i represents the cross section for collisions with $|\Delta M_J\Omega| = i$. Hence, the cross sections for

collisions which reorient the OH molecule by one quantum are about a factor of 6 smaller than the total elastic cross sections, but a factor of 2 larger than cross sections for a larger reorientation. M_J unresolved quantum scattering calculations indicate that the elastic cross section is about 189 \AA^2 [13]. This cross section should be equal to the sum of σ_0 and $\sigma_{6/4}$ in our experiment. This provides an estimate of the absolute values of the reorientation cross sections of σ_0 , $\sigma_{6/4}$, $\sigma_{12/4}$, $\sigma_{18/4} = 164$, 25, 12, and 13 \AA^2 , respectively.

Since the bandwidth of the laser is much smaller than the Doppler width of the scattered molecules, it is possible to estimate the differential cross sections. This estimate is given by the scattering angle θ_{FWHM} corresponding to the points at FWHM of the Doppler profile (Table I). For all final states, the scattering distribution peaks in the forward direction, however, the scattering angle increases as $\Delta(M_J\Omega)$ increases from 0 to $\frac{18}{4}$. This is because for a larger change in quantum numbers, a stronger interaction is needed (or a smaller impact parameter) which will also lead to a larger deflection of the molecules.

The steric asymmetry has been measured for both scattering out of the initial states and for scattering into the final states. For collisions of molecules in the $-\frac{9}{4}$ state there is no difference between collisions at the O end or the H end. When a molecule in the $-\frac{3}{4}$ state collides, however, the fractional loss is larger for collisions at the O end. If radicals are scattered into the $M_J\Omega = +\frac{9}{4}$ or $-\frac{9}{4}$ states, there is a small preference for collisions at the H end, while there is a clear preference for O-end collisions in scattering processes to the $M_J\Omega = +\frac{3}{4}$ or $-\frac{3}{4}$ states. A preference for O-end collisions was also observed for rotationally inelastic collisions to low J states [9]. If a steric asymmetry is present, one would expect larger values for collisions involving $|M_J\Omega| = \frac{9}{4}$ states compared to $|M_J\Omega| = \frac{3}{4}$ states since the degree of orientation is much larger for molecules with $|M_J\Omega| = \frac{9}{4}$. Within the accuracy of our experiment the Doppler profile of the scattered molecules was the same for collisions at the O end and the H end of the molecules, indicating that the differential cross section is similar for H-end and O-end collisions.

To conclude, the results presented in this Letter describe the first scattering experiments on reorientation of the molecular axis. The reorientation cross section for $\Delta M_J\Omega = \frac{6}{4}$ is 25 \AA^2 ; the cross sections for larger reorientation are a factor of 2 smaller. Collisions which induced a larger reorientation also induced a larger scattering angle. The fractional loss for collisions in the $-\frac{9}{4}$ state was found to be slightly larger than for collisions in the $-\frac{3}{4}$ state. The fractional loss does not depend on the initial ori-

entation with respect to the collision partner. However, the state-to-state cross sections are larger for collisions at the O end for final states with $|M_J\Omega| = \frac{3}{4}$, while H-end collisions are preferred in transitions to the $|M_J\Omega| = \frac{9}{4}$ states. The technique used in this experiment makes it possible to measure orientation effects in molecular processes on a state-to-state basis and to obtain information on the differential cross section. This method has been demonstrated for rotationally elastic collisions of OH + Ar but it can equally well be applied to the study of inelastic and reactive collisions and photodissociation processes. Also other systems can be studied in detail using this method provided that the primary molecule can be electrostatically state selected. The study of orientation effects provides highly state resolved information, which can be compared with quantum scattering calculations without the need to average over M_J quantum states and orientations.

We wish to thank E. van Leeuwen for his expert technical support and Dr. N. Dam for stimulating discussions.

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