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I. INTRODUCTION

Reactions of the OH radical with hydrogen halides (HCl, HBr, HI) play a crucial role in the atmospheric chemistry as the produced halogen atoms contribute significantly to the destruction of ozone. Various kinetic studies on these systems have been reported, resulting in the determination of reaction rate constants as a function of temperature. The intermolecular potentials are, however, less well known. Among these systems the OH–HCl one has been studied most extensively. We recently performed state-to-state inelastic scattering measurements in which the OH radical was either oriented or not with respect to the HCl molecule. The obtained state-to-state cross sections were compared with the results of reduced dimensionality calculations using a two-dimensional (2D) or four-dimensional (4D) potential energy surface (PES).

In this article, we report measurements on (non-) oriented OH radicals in collisions with HBr. Compared to the interaction of OH with HCl, HBr is predicted to be more reactive, presenting a rate constant at room temperature about one order of magnitude larger, $1.1 \times 10^{-11}$ cm$^3$ s$^{-1}$, and a two times higher exothermicity, 131.5 kJ/mol. Clary et al. reported quantum scattering calculations using rotating bond approximation and treating explicitly the bending vibration and local OH stretching vibration in H$_2$O, the vibration of HBr and rotation of OH. For both reactants in the ground electronic and vibrational state and also ground rotational state for the hydroxyl radical, the resulting OH+HBr reaction cross section was 28 Å$^2$ at a collision energy of 0.09 eV; at a similar collision energy the vibrational population of the H$_2$O product measured by IR chemiluminescence was about 0.09 eV; at a similar collision energy the vibrational population of the H$_2$O product was predicted to be (1,1), (0,2), (2,1), (1,2) in order of decreasing cross sections, where the first quantum number refers to the bending vibration and the second to both stretching types. These results were found to be in general agreement with the vibrational distribution of the H$_2$O product measured by IR chemiluminescence by Butkovskaya and Setser. The calculations of Clary et al. were based on an approximate PES. The authors found a strong dependence of the cross sections with the rotational quantum number of the OH molecule. In a direct dynamics study Liu et al. found that the OH+HBr reaction proceeds via a hydrogen bounded complex and subsequently a transition state. An energy barrier of about 310 cm$^{-1}$ was obtained in contrast to Clary et al. and Nizamov et al. who found a potential well instead of a reaction barrier, equal to 601.6 and 622.6 cm$^{-1}$, respectively. Regarding the inelastic channel no calculations have been reported thus far.

Besides the chemical nature and collision energy, the internal energy and the impact geometry are factors that determine the output of a scattering process. Taking advantage of the polar properties and $^3\Pi$ symmetry of the hydroxyl radical, electrostatic field methods can be used to select and spatially focus only the molecules in a specific internal state, in the present case $X^2\Pi_{3/2}, v=0, J=3/2, M_J=3/2, f$. This enables the study of state-to-state rotational excitation. In addition, it is possible by using electrostatic fields to orient these molecules with either the O or H side directed towards...
II. EXPERIMENTAL PROCEDURE

A detailed description of the experimental setup is given in previous reports. Briefly, a crossed beam machine pumped to $10^{-7}$ - $10^{-8}$ Torr is provided with two 50 $\mu$s (full width at half maximum) molecular pulses (Jordan) at a repetition rate of 10 Hz. The OH beam is produced by expanding 3% H$_2$O in Ar through one of these valves with a nozzle opening of 0.2 mm diameter. The backing pressure is 600 Torr. At 15 mm from the nozzle a stainless steel ring with an inner diameter of 3 mm is kept at $-4$ kV, producing an electrical discharge in the expanding mixture. After passing a skimmer with an opening of 2.5 mm diameter and at a voltage of $-300$ V to deflect the ions formed in the discharge, the beam molecules enter a double hexapole state selector. The hexapole voltage is set to focus the OH molecules in the state $\Omega = 3/2$, $J = 3/2$, $M_J = 3/2$, $f$ into the region of collisions with the secondary beam. A 2 mm diameter beam stop is placed on the molecular beam axis in front of the state selector to block the molecules, which fly along the central axis and do not experience any field for the selection. Half way in the state selector the OH molecules in the $J = 3/2$, $M_J = 3/2$ state are focused for the first time. This enables the blocking of OH molecules in the other low field seeking states (mainly $J = 3/2$, $M_J = 1/2$) by inserting a diaphragm with a diameter of 3.5 mm. As a result, the distribution of the hydroxyl radical population in the collision region is 94% in the $\Omega = 3/2$, $J = 3/2$, $f$ state, 4% in the $\Omega = 3/2$, $J = 5/2$, $f$ state, and less than 0.5% in each other rotational state. The measured cross section for the transition to the $\Omega' = 3/2$, $J' = 5/2$, $f$ final state has been corrected for the initial population of this state assuming that the relative depletion of population by out-scattering is the same for $J = 3/2$ and $J = 5/2$ states.

The secondary beam is formed in the supersonic expansion of 1 bar pure HBr gas through a 0.5 mm diameter nozzle. At 30 mm downstream of the nozzle and 60 mm before the collision center a 3 mm diameter skimmer is located. Analysis of resonance enhanced multiphoton ionization (REMPI) spectra of various rotational branches of the excitation transitions to the $g^3\Sigma^-$ $(0-0)$, $f^3\Delta_2$ $(0-0)$, and $I^3\Delta_2$ $(0-0)$ states revealed a rotational cooling of the $X^1\Sigma^+$ state down to $19 \pm 3$ K, as shown in Fig. 1. The isotope shifts corresponding to H$^{79}$Br (50.7%) and H$^{81}$Br (49.3%) are not resolved. The backing pressure of the secondary beam gas has been chosen to cause not more than 10% out-scattering of the initial population of OH in the $\Omega = 3/2$, $J = 3/2$, $f$ state, in order to maintain a single collision regime. The collision energy of OH seeded in Ar colliding at a right angle with the pure HBr beam is estimated to be $750 \pm 190$ cm$^{-1}$.

For the measurements of the steric asymmetries an orientation field is created in the collision region by four parallel rods biased in pairs in order to induce a 7.5 kV/cm field parallel or antiparallel to the relative velocity vector of the molecular beams. By means of the Stark effect the combination of the electrostatic fields of the hexapole and the orientation rods assures that for one polarity of the four rods the O side of the molecules is oriented towards the HBr molecules and the H side for the reversed polarity. Preference for one of these orientations results in a larger measured scattering cross section. A detailed description of the theory of the OH state selection and subsequent orientation is given in other preceding reports.

The A-doublet state resolved population distribution is probed by saturated LIF by exciting the $A^3\Sigma^+ - X^1\Pi$ transition at 308 nm. The second harmonic generation of a Nd:YAG (yttrium aluminum garnet) laser with 5 ns pulse and 10 Hz repetition rate is used to pump a dye laser (Lambda Physik model Scanmate 2) operating with Sulfonadine SR 640; the doubled output is set at 0.5 - 0.8 mJ/pulse in order to prevent line broadening and still saturate the absorption. The laser bandwidth is 0.45 cm$^{-1}$, which allows the spectral resolution of all measured OH transitions except for the Q$_2$ (2) and Q$_2$ (3) transitions. The spatial spreads of the OH and HBr beams at the collision and detection region are 2 and 9 mm, respectively. The laser beam size is 4 mm in diameter at the crossing of the molecular beams. The Q$_1$ and P$_1$ transitions are used to probe the population of the $^3\Pi_{3/2}$, $J = 3/2 - 11/2$, $f$ and $J = 3/2 - 9/2$, $e$ states, respectively; whereas the P$_2$ and Q$_2$ transitions are used for the $^3\Pi_{1/2}$, $J = 3/2$, $5/2$, $f$ and $J = 1/2 - 7/2$, $e$ states, respectively; for the population of the $^3\Pi_{1/2}$, $J = 1/2$, $f$ state the P$_{13}$ (1) line has been used. A system
of two lenses and a UG-11 filter is used to collect the fluorescent light onto the photomultiplier tube (EMI 9235 QB). The laser beam is passed through light baffles before and after the detection region and is dumped into a Wood's horn in order to reduce the background due to laser beam. Gated boxcar signals are accumulated over 2000 shots with secondary valve modulation every 128 shots during which the gas pulse is delayed or not by 1 ms with respect to the other beam. Subtraction of the modulated signals gives the effect of the collisions: an in- or outscattering signal. For the oriented scattering a measurement cycle of 1000/2000/1000 shots is applied with alternating polarity between the rods, +/−/+ or −/+/, in order to compensate for the experimental drifts in laser energy and alignment. 10–80 measurements have been used for each rotational level to deduce the mean value and its accuracy by weighted averaging (Fig. 2).

III. RESULTS AND DISCUSSION

A. State-to-state cross sections

The differences in final internal state energies do not imply significant differences in the residence time of the OH molecules in the detection volume. In the geometry of these experiments the flux-to-density transformation for the LIF signal to molecular density conversion has been considered negligible within the experimental accuracy. In order to correct for the different degeneracy factors of the initial and final states the fluorescence signal was divided by the excitation rate. 17

\[
ER = \frac{(2J_{\text{main}}' + 1) + (2J_{\text{sat}}' + 1)}{(2J_{\text{main}} + 1) + (2J_{\text{sat}} + 1) + (2J'' + 1)},
\]

where the labels \textit{main} and \textit{sat} refer to the main or satellite spectroscopic lines excited together within the laser bandwidth and \(J'\) and \(J''\) designate the total angular momentum quantum numbers for the fluorescent excited state and the ground state, respectively. In the absence of the calculated cross sections to scale with, the relative state-to-state inelastic cross sections for the transitions \(\Omega'', J'', \epsilon'' \rightarrow \Omega', J', \epsilon'\) have been determined using the following formula:

\[\sigma_{\text{rel}}(\Omega', J', \epsilon') = \frac{\text{Inscattering}(\Omega', J', \epsilon')}{\text{Outscattering}(\Omega'', J'', \epsilon'')} \times 100\% . \tag{2a}\]

Here \(\Omega\) is the projection of the total angular momentum \(J\) onto the internuclear OH axis and \(\epsilon\) corresponds to the \(\Lambda\)-doublet state \(e\) or \(f\) symmetry. For \(\Omega = \frac{3}{2}\), \(f\) and \(\Omega = \frac{1}{2}\), \(e\) states the half filled electronic \(\pi\) orbital is antisymmetric with respect to a reflection in the molecular rotation plane, \(e\), and the symmetry with respect the reflection into the molecular rotation plane, \(e\), are specified for each of the rotational levels depicted.

\[
\text{Inscattering}(\Omega', J', \epsilon') \propto \int_{\text{Det Vol}} \sigma_{\text{inelastic}}(\Omega'', J'', \epsilon'' \rightarrow \Omega', J', \epsilon') v_{\text{relative}}(\text{OH} + \text{HBr}) dV,
\]

\[
\text{Outscattering}(\Omega'', J'', \epsilon'') \propto \int_{\text{Outside Det Vol}} \sigma_{\text{elastic}}(\Omega'', J'', \epsilon'') v_{\text{relative}}(\text{OH} + \text{HBr}) dV
\]

\[
+ \int_{\text{All space}} \left( \sum_{\Omega', J', \epsilon'} \sigma_{\text{inelastic}}(\Omega'', J'', \epsilon'' \rightarrow \Omega', J', \epsilon') + \sigma_{\text{reactive}} \right) v_{\text{relative}}(\text{OH} + \text{HBr}) dV,
\]
TABLE I. Relative state-to-state cross sections \( \sigma_{rel} (\%) \) for inelastic scattering of OH (X \( ^3\Pi, v=0, J=3/2, f \)) in collisions with pure HBr (X \( ^3\Sigma^-, v=0, J<4 \)) at 750 cm\(^{-1} \) collision energy.

<table>
<thead>
<tr>
<th>Final state ( \Omega' )</th>
<th>J</th>
<th>f</th>
<th>e</th>
</tr>
</thead>
<tbody>
<tr>
<td>3/2</td>
<td>3/2</td>
<td>...</td>
<td>51.90±0.88</td>
</tr>
<tr>
<td>5/2</td>
<td>5.73±0.35</td>
<td>5.48±0.52</td>
<td></td>
</tr>
<tr>
<td>7/2</td>
<td>2.55±0.31</td>
<td>2.15±0.40</td>
<td></td>
</tr>
<tr>
<td>9/2</td>
<td>1.39±0.34</td>
<td>1.50±0.40</td>
<td></td>
</tr>
<tr>
<td>11/2</td>
<td>0.62±0.32</td>
<td>...</td>
<td></td>
</tr>
<tr>
<td>1/2</td>
<td>1/2</td>
<td>1.35±0.27</td>
<td>1.84±0.24</td>
</tr>
<tr>
<td>3/2</td>
<td>1.47±0.28</td>
<td>2.45±0.30</td>
<td></td>
</tr>
<tr>
<td>5/2</td>
<td>0.91±0.60</td>
<td>...</td>
<td></td>
</tr>
<tr>
<td>7/2</td>
<td>...</td>
<td>0.78±0.18</td>
<td></td>
</tr>
</tbody>
</table>

\( \Omega = 1/2, J = 3/2 \) and \( 5/2, e \) state populations are probed by transitions which are not separated within the laser bandwidth.

\( \sigma_{elástico}, \sigma_{inelástico} \) and \( \sigma_{reaction} \) are absolute cross sections. In these expressions it is assumed that all OH molecules are in the initial state \( \Omega'', J'', e'' \). The measured inelastic scattering \( \sigma_{rel}(\Omega', J', e') \) signal, consists of fluorescence emitted by the molecules scattered to the final \( \Omega', J', e' \) state and activated by the resonant laser radiation. The intersection of the laser beam and scattered OH molecular beam forms the detection volume. The larger the detection volume, the smaller the contribution of the elastically scattered molecules to the inelastic cross section, \( \sigma_{rel}(\Omega', J', e') \). The amount of molecules found back in other internal states is

\[
\sum_{\Omega'', J'', e''} \sigma_{rel}(\Omega', J', e') \propto 80 \pm 2 \%
\]

while for the OH–HBr system, at 750 cm\(^{-1} \) collision energy, the corresponding amount is

\[
\sum_{\Omega', J', e'} \sigma_{rel}(\Omega', J', e') \propto 80 \pm 2 \%
\]

The missing amount of molecules is thus correlated to (in) elastic scattering outside the probe laser beam, possible reactive channels, and not measurable inelastic scattering to higher energy internal states; these total contributions are equal within the experimental accuracy for scattering by HBr and by HCl.

The results for the OH–HBr relative state-to-state inelastic cross sections are listed in Table I. As a result of the collision with the HBr molecules, the OH \( ^3\Pi_{1/2}, v=0, J =3/2, f \) molecules are rotationally excited to both spin-orbit states \( ^3\Pi_{3/2} \) and \( ^3\Pi_{1/2} \), conserving or changing the state parity, or are slightly deexcited to the lower rotational state \( \Omega' = 3/2, J' = 3/2, e \), changing only the parity. The molecules excited to the highest rotational energy state, \( \Omega' = 3/2, J' = 11/2, f \), amount to a small percent out of the total scattered molecules, 0.6%. For this excitation the conversion of the collision kinetic energy to internal rotation energy is maximal, 546 cm\(^{-1} \). The largest cross section, 51.9±0.9%, is obtained for the parity changing transition, for which the energy change is only 0.05 cm\(^{-1} \), the A-doublet splitting of the \( J=3/2 \) state. The large value of the cross section for the transition to the \( \Omega'=1/2, J'=3/2 \) and \( 5/2, e \) states is due to the fact that it includes contributions from excitations to both rotational states, probes by transitions unresolved within the laser bandwidth.

The outscattering \( \sigma_{rel}(\Omega', J', e') \) signal, which is the denominator in the expression \( (2a) \) of the relative state-to-state cross section, is assumed to be the same for all the final states probed, but can differ from system to system. For the comparison among OH–X systems, the relative cross sections, \( \sigma_{rel}(\Omega', J', e') \), have been divided by the absolute cross section for the scattering to one particular state, as chosen, \( \Omega' = 3/2, J' = 3/2, e \). The results for the OH–HBr experiments at a collision energy of 920 cm\(^{-1} \), \( \sigma_{rel}(\Omega', J', e') \), have been divided by the relative cross section for the scattering to one particular state, as chosen, \( \Omega' = 3/2, J' = 3/2, e \), and the product \( \sigma_{rel}(\Omega', J', e') \) has been considered constant over the entire detection volume. Hence, the resulting ratios, \( \rho(\Omega', J', e') \) (\%), are the ratios of the absolute state-to-state inelastic cross sections for the scattering to each probe state to the absolute inelastic cross section for the scattering to the \( \Omega' = 3/2, J' = 3/2, e \) state. They are shown graphically in Fig. 3 for the OH–HBr system at 750 cm\(^{-1} \) collision energy and OH–HCl at 920 cm\(^{-1} \). As shown, the ratios are larger for the OH–HBr system for many of the higher excitations. Relative to the amount of molecules that are slightly deexcited to the parity changing state, the amount of molecules rotationally excited decreases with increasing rotational quantum number and this trend is very similar for both halogen hydride partners. Another similar feature is that no propensity with respect to the A-doublet parity is measured within the experimental accuracy. For most other systems studied thus far such as OH–He, –N\(_2\), –CO, –Ar, and –CO\(_2\), a clear propensity for the \( \Omega' = 3/2, J' = 5/2, e \) state is revealed. The \( \Omega' = 3/2, f \) states correspond to the antisymmetric configuration with the unfilled electronic \( \pi \) orbital perpendicular to the molecular rotation plane. In collisions with HCl and HBr the molecules exhibit no tendency to keep this configuration above, changing it into the symmetric configuration with the unfilled orbital in the plane of molecular rotation. Probably the long-range dipole-dipole or dipole-quadrupole interactions are dominant over the short-range dispersion forces, which may differ for the symmetric and antisymmetric configurations.

B. Effects of the molecular orientation

The oriented scattering measurements were performed using an electrostatic field along the direction of the relative velocity vector of the two molecular beams. By changing the polarity of the rods the orientation of the OH molecules was alternated such that OH collides with the HBr molecule with either the O or the H side. A quantification of the degree of orientation is given by the average value of the angle between the molecular axis and the axis of the external field.\( ^{31,22} \)
The state-to-state steric asymmetries used to quantify the orientation effect on the scattering process are defined as follows:

\[ S(\Omega', J', e') = \frac{\sigma_{\text{OH} - X} - \sigma_{\text{H} - X}}{\sigma_{\text{OH} - X} + \sigma_{\text{H} - X}} \times 100 \% , \]  

where \( \sigma_{\text{OH} - X} \) or \( \sigma_{\text{H} - X} \) represents the state-to-state cross section for the scattering of the OH molecules oriented with the \( \text{OH} \) or the \( \text{H} \) side, respectively, towards the collision partner. A positive steric asymmetry indicates the preference for scattering at the \( \text{OH} \) side and alternatively, a \( \text{H} \) side preference corresponds to a negative value of the steric asymmetry.

Since both molecules involved in this experiment have a large dipole moment (0.82 D for HBr and 1.66 D for OH), a strong anisotropy of the PES is expected and thus strong steric asymmetries. The results for the measured steric asymmetries corresponding to state-to-state rotationally inelastic scattering of OH by HBr are presented in Table II. Figure 4 shows the graphical comparison with the steric asymmetries measured for scattering of OH by HCl. As it can be seen, these asymmetries are small in contrast to the expectations. For spin-orbit conserving transitions a trend to larger positive values with increasing rotational excitation is visible. An increase of the steric asymmetries with decreasing cross sections has been observed before in the case of OH–Ar and OH–CO scattering. For the spin-orbit changing transitions the experimental accuracies are low and no clear trend with \( J' \) is observed. When comparing with HCl collisions there are no significant differences except for the transitions to the \( \Omega' = 3/2, J' = 5/2 \) and 7/2, \( f \) states. Here relatively large negative steric asymmetries are measured for OH–HCl whereas the steric asymmetries are nearly zero for OH–HBr. A possible explanation for the negative values in the case of...
FIG. 4. State-to-state steric asymmetries \( S(\%) \) for (a) spin-orbit conserving transitions and (b) spin-orbit changing transitions for scattering of OH \((X^2\Pi, v=0)\) \( \Omega^\prime=3/2, J^\prime=3/2, f \) by HBr at 750 cm\(^{-1}\) collision energy (squares) and by HCl at 920 cm\(^{-1}\) collision energy (circles).

HCl collisions is the influence of the HO–HCl van der Waals well\(^{11}\), which depth estimated using different levels of theory\(^{12,13,23,24}\) is in the range of 870–1900 cm\(^{-1}\). For the HO–HBr hydrogen bond complex Liu et al. calculated a well depth of about 600 cm\(^{-1}\).\(^{9}\) We may attribute this less deep potential well to a weaker intermolecular interaction since HBr has a smaller electric dipole moment than HCl and is a larger molecule. Both systems exhibit H–O–H bond configurations very close to the stable water molecule geometry. Thus, OH molecules coming with the O side towards the halogen hydride are relatively more preferred for the complex formation channel. After the predissociation of the complex, the OH fragment population may undergo redistribution over rotational, symmetry and spin-orbit internal states within the available energy. This is consistent with the slight positive steric asymmetries for higher rotational excitation and several spin-orbit changing transitions. The smaller steric asymmetries for OH+HBr may be related to the shallower van der Waals well. Another interesting difference between the PESs of OH–HCl and OH–HBr is the barrier height of the reactive channel: 300–800 cm\(^{-1}\) for OH+HCl (Refs. 23–27) and 20–311 cm\(^{-1}\) (Refs. 8 and 9) or no barrier at all\(^{12}\) for OH+HBr. The OH+HBr collision energy overcomes by far the barrier of 311 cm\(^{-1}\). Noting the very high exothermicity one may expect a fast reactive channel. However, the higher reactivity of OH+HBr relative to OH +HCl is not reflected in the magnitude of the inelastic cross sections and it does not explain the low steric asymmetries for the OH–HBr inelastic collisions. The explanation awaits results of quantum scattering calculations and of complementary experiments. Experiments to measure the Br reaction product are in progress.

IV. SUMMARY

State-to-state rotationally inelastic cross sections of the hydroxyl radical in collisions with hydrogen bromide have been measured in a crossed molecular beam experiment. Out of the 94% pure initial state, \(^2\Pi_{3/2}, v=0, J=3/2, M_J=3/2, f\), the OH molecules are scattered into different excited states corresponding to changes of up to three rotational quanta, spin-orbit component, and/or molecular symmetry. While the largest cross section was measured for the A-doublet transition, the general trend found is a fast decrease of the cross section with increasing excitation. Different cross sections are measured when changing the OH molecule orientation prior to the collision so that the impact takes place at the O side or the H side, as a result of sampling parts of the intermolecular PES exhibiting a different anisotropy. Large differences in steric asymmetries for OH–HCl and OH–HBr systems are measured for the parity and spin-orbit conserving transitions, the origin of which is not yet clear.

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27 IUPAC database (Subcommittee for Gas Kinetics Data Evaluation), http://www.iupac-kinetic.ch.cam.ac.uk