State-to-state inelastic scattering of OH by HI: A comparison with OH–HCl and OH–HBr

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Relative state-to-state cross sections and steric asymmetries have been measured for the scattering process: OH (\(X^2 \Pi_{3/2}, v=0, J=3/2, M_J=3/2, f\)) + HI (\(1 \Sigma, v=0, J<4\)) \(\rightarrow\) OH (\(X^2 \Pi, v=0, \Omega=1/2, J=1/2\) or \(5/2\) and \(\Omega=3/2, J=3/2\) or \(9/2\) or \(f\)) + HI, at 690 cm\(^{-1}\) collision energy. Comparison with the previously studied systems OH–HCl and OH–HBr reveals relevant features of the potential energy surfaces of these molecular systems. Some measured differences concerning the internal energy distribution after collision and the propensities for the impact with one or the other side of the OH molecule in scattering by HCl, HBr, and HI molecules are discussed. © 2007 American Institute of Physics. [DOI: 10.1063/1.2715930]

I. INTRODUCTION

The interaction of the hydroxyl radical with hydrogen iodide is expected to cause the main gas-phase loss of HI in the lower marine atmosphere and to play an important role in the chemistry of iodine, which can efficiently catalyze ozone destruction in the stratosphere\(^1\) and marine troposphere.\(^2\) The OH–HI molecular interaction potential, which determines the interplay between elastic, inelastic, and reactive processes involved in the collision of these two molecules, is not well known so far. The present experimental study on state-to-state inelastic scattering of the hydroxyl radical by collisions with the HI molecule can be combined with the previous work on the kinetics of the OH+HI reaction,\(^4\) to enrich the range of tools for probing the potential energy surface (PES) of this system. This work follows previous investigations on the rotational inelastic scattering of the OH molecule by collisions with two other halides, HCl (Refs. 10 and 11) and HBr.\(^12\)

The reactive channel (OH+HI \(\rightarrow\) H\(_2\)O+I) can be characterized by its energy disposal, activation energy, thermal rate constants, and their temperature dependence as given by the results of various flow-reactor experiments.\(^4\) The reported kinetic studies of the OH+HI reaction indicate a large rate coefficient and no significant activation barrier. Among the three HI halides, X=Cl, Br, and I, the HI molecule is found to have the highest room temperature rate for the reaction with the OH radical, in the range of 2\(\times\)10\(^{-11}\)–7\(\times\)10\(^{-11}\) cm\(^3\) s\(^{-1}\), and the highest reaction exothermicity, 199.6 kJ/mol. The correlation between the bond energy of these halides and the rate constants for their reaction with OH molecules indicates that the reactions proceed via H atom abstraction.\(^8\) Besides their size, the three mentioned halides differ also by electric dipole moments, averaged quadrupole moments, and polarizabilities (Table I), and subsequently, the OH–HX interaction potentials have different features that measurable quantities are expected to reflect. Indeed, Butkovskaya and Setser\(^12\) measured by IR chemiluminescence the vibrational distribution of H\(_2\)O product in a fast flow reactor at room temperature and found that 36% of the available energy of the OH+HI reaction goes into the vibration excitation of H\(_2\)O, while for the OH+HBr reaction 61% of the available energy is transferred to internal vibration energy of water, and no vibrational energy is found for the water product of the OH+HCl reaction.\(^13\) The energy disposal shows that the dynamics of these reactions are different.

Besides the direct H atom abstraction an alternative mechanism is likely to occur, in which the OH radical ini-

<table>
<thead>
<tr>
<th>HX</th>
<th>Mass (amu)</th>
<th>Dipole(^a) (D)</th>
<th>Quadrupole(^b) (D (\hbar))</th>
<th>Polarizability(^c) ((\AA^3))</th>
<th>Electronegativity(^d) atom X</th>
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</thead>
<tbody>
<tr>
<td>OH</td>
<td>17</td>
<td>1.66</td>
<td>1.4</td>
<td>1</td>
<td>3.44</td>
</tr>
<tr>
<td>HF</td>
<td>20</td>
<td>1.82</td>
<td>2.1</td>
<td>0.7</td>
<td>3.98</td>
</tr>
<tr>
<td>HCl</td>
<td>36.5</td>
<td>1.08</td>
<td>3.6</td>
<td>2.4</td>
<td>3.16</td>
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<tr>
<td>HBr</td>
<td>81</td>
<td>0.83</td>
<td>4.2</td>
<td>3.3</td>
<td>2.96</td>
</tr>
<tr>
<td>HI</td>
<td>128</td>
<td>0.38</td>
<td>6</td>
<td>6.7</td>
<td>2.66</td>
</tr>
</tbody>
</table>

\(^a\)Experimental values given in NIST database.
\(^b\)Calculated zz diagonal term of the electric quadrupole moment tensor given in NIST database.
\(^c\)Calculated diagonal-term average of the polarizability tensor given in NIST database (Ref. 22).
\(^d\)Pauling scale, in which the electronegativity is 2.20 for the H atom.
tially attacks the halogen atom end of H'X, after which the H' atom migrates to the oxygen atom and H2O is formed. A similar hydrogen atom addition-migration mechanism (the addition to the I, Br, or Cl atom followed by the migration to the F atom) has been observed for the H+FI → HF+I and H+FBr → HF+Br and H+FCl → HF+Cl reactions which present microscopic branching, i.e., “direct” and “migratory” dynamics are present as distinct routes to the same reaction products. The migration of the H atom from a halogen atom, I, Br, and Cl, to a more electronegative one, F, was found to lead to a rotationally hotter HF product. A similar migration of the H' atom from a halogen to the O atom of the hydroxyl radical may lead to higher population of the H2O product in the bending mode. Butkovskaya and Setser measured the fraction of energy into the bending mode relative to the total vibration energy as 0.30 for water produced by OH+HBr and 0.46 for water produced by OH+HI, and correlated the increase of this fraction with the contribution of the addition-migration reaction mechanism. The internal and kinetic energy distribution of the reaction products and the cross sections for the reactive and inelastic processes are dependent on the interaction mechanisms involved and their competition.

In the present experiment the inelastic collision channel is characterized by state-to-state cross sections for the rotationally inelastic scattered OH molecules and by the steric asymmetries, which indicate the effect of the orientation of the radical with the O side or with the H side toward the collision partner on the state-to-state cross sections, thus probing the anisotropy of the OH–HI PES. Unfortunately, no other experimental or theoretical results on inelastic scattering of OH by HI have been reported thus far. We can thus only compare the measured relative cross sections and steric asymmetries with the corresponding results for the OH–HCl and OH–HBr systems. This, however, reveals some interesting differences pointing at different features of the potential energy surfaces.

II. EXPERIMENTAL PROCEDURE

A detailed description of the experimental setup is given in previous reports. Two pulsed 50 μs full width at half maximum duration molecular beams (Jordan) operating at a repetition rate of 10 Hz expand supersonically in perpendicular directions. The OH beam is produced by an electrical discharge in an expanding mixture of 3% H2O in Ar through a nozzle opening of 0.2 mm diameter. The backing pressure is 600 Torr. A skimmer with an opening of 2.5 mm, a beam stop, and a combination of two electrostatic hexapoles separated by a diaphragm of 3.5 mm in diameter form a state selector for OH molecules in the upper \( J = 3/2 \) A-doublet state. In the collision region, 37 cm downstream of the valve, the population distribution of the hydroxyl radicals is 93% in the \( \Omega = 3/2, J = 3/2, \epsilon = f \) state, 4% in the \( \Omega = 3/2, J = 5/2, \epsilon = f \) state, and less than 0.5% in each other rotational state. Here \( \Omega \) is the projection of the total angular momentum \( J \) onto the internuclear OH axis and \( \epsilon \) labels the \( e \) or \( f \) symmetry of the A-doublet state.

The HI valve is provided with a 0.5 mm diameter nozzle positioned at about 90 mm in front of the collision center. By using resonance enhanced multiphoton ionization (REMPI) via the \( f^3 \Sigma, v=0 \) state we found a rotational cooling of the HI molecules in the \( v=0 \) ground electronic state down to 17±4 K, as shown in Fig. 1. The collision energy of OH molecules seeded in Ar colliding at right angles with the pure HI molecular beam is 690±190 cm\(^{-1}\). In order to maintain a single collision regime and to decrease the presence of HI clusters, the backing pressure was kept at 1.1 bars, causing about 6% outscattering of the initial OH population of the \( \Omega = 3/2, J = 3/2, f \) state.

For the measurement of steric asymmetries an electrostatic 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. For one polarity of the four rods the O side of the molecules is oriented toward the HI molecules,
whereas this is the case for the H side at the reversed polarity. Preference for one of these orientations results in a larger measured scattering cross section.

The A-doublet state resolved population distribution is probed by saturated laser induced fluorescence by exciting the A (2Σ)→X (2Π) transition at 308 nm. The 5 ns duration laser pulses, at a repetition rate of 10 Hz, with an energy of 0.5–0.8 mJ and spectral bandwidth of 0.45 cm⁻¹, travel perpendicularly to the molecular collision plane. The spatial spreads of the OH and HI beams at the collision and detection regions are 2 and 9 mm, respectively. At the crossing of the molecular beams the laser beam is 4 mm in diameter.

III. RESULTS

A. State-to-state cross sections

State-to-state cross sections were determined for OH \(\Omega', J', e'\)→\(\Omega'', J'', e''\) transitions due to the collisions with HI molecules. The initially selected state is characterized by the quantum numbers \(\Omega''\) and \(J''\), where both are equal to 3/2, and \(e''=f\). The half filled electronic \(\pi\) orbital is more perpendicular to the OH rotation plane for the \(\Omega'=3/2, f\) and \(\Omega'=1/2, e\) states and is more in the rotation plane for the \(\Omega'=3/2, e\) and \(\Omega'=1/2, f\) states. The total parity is given by \((-1)^{J'+1/2}\) for the \(f\) states and \((-1)^{J'-1/2}\) for the \(e\) states. Due to the lack of differential cross sections needed to characterize the scattering of this molecular system, the flux to density transformation is not taken into account in the data analysis. Nevertheless, the differences in final internal state energies do not imply significant differences in the residence time of the OH molecules in the detection volume and the flux to density transformation is considered to not have a major effect on the presented results at the present experimental accuracy. For each collision induced transition \(\Omega'', J'', e''\)→\(\Omega', J', e'\) the relative state-to-state inelastic cross sections are given by

\[
\frac{\sigma_{\text{rel}}(\Omega', J', e')}{\sigma_{\text{rel}}(\Omega'', J'', e'')} = \frac{F_{\text{in}}(\Omega', J', e')}{F_{\text{out}}(\Omega'', J'', e'')} \times 100(\%),
\]

with \(F_{\text{in}}(\Omega', J', e')\) the fluorescence signal due to the increase of the \(\Omega', J', e'\) internal state population by inelastic and \(F_{\text{out}}(\Omega'', J'', e'')\) the decrease of the signal due to the OH molecules scattering out of the \(\Omega'', J'', e''\) internal state, initially populated:

\[
F_{\text{in}}(\Omega', J', e') = \int_{\text{Det Vol}} \sigma_{\text{inelastic}}(\Omega'', J'', e''→\Omega', J', e') \rho_{\text{relative}}^{\text{OHH}}(v) dv,
\]

\[
F_{\text{out}}(\Omega'', J'', e'') = \int_{\text{Det Vol}} \sigma_{\text{inelastic}}(\Omega'', J'', e''→\Omega', J', e') \rho_{\text{relative}}^{\text{OHH}}(v) dv,
\]

where \(n\) is the number density, \(v_{\text{relative}}\) the average relative velocity of the molecular beams, and \(\sigma_{\text{inelastic}}\) the absolute inelastic cross section. 6% of the initial \(\Omega'=3/2, f\) state population was outscattered by collisions. Out of these 6% scattered molecules, 62% were detected in different rotational states.

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\]

with \(F_{\text{in}}(\Omega', J', e')\) the fluorescence signal due to the increase of the \(\Omega', J', e'\) internal state population by inelastic and \(F_{\text{out}}(\Omega'', J'', e'')\) the decrease of the signal due to the OH molecules scattering out of the \(\Omega'', J'', e''\) internal state, initially populated:

\[
F_{\text{in}}(\Omega', J', e') = \int_{\text{Det Vol}} \sigma_{\text{inelastic}}(\Omega'', J'', e''→\Omega', J', e') \rho_{\text{relative}}^{\text{OHH}}(v) dv,
\]

\[
F_{\text{out}}(\Omega'', J'', e'') = \int_{\text{Det Vol}} \sigma_{\text{inelastic}}(\Omega'', J'', e''→\Omega', J', e') \rho_{\text{relative}}^{\text{OHH}}(v) dv,
\]

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The results for the OH–HI relative state-to-state cross sections are listed in Table II. In the collisions with HI, the OH molecules in the state \(^3 \Pi_{1/2}, v=0, J=3/2\), \(f\) 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 A-doublet state \(\Omega'=3/2, J'=3/2, e\), changing only the parity. The highest rotational energy state observed, \(\Omega'=3/2, J'=9/2\), \(f\), is populated by a very small amount of the scattered molecules, \((81\pm2)\%\). For these molecules the conversion of collision kinetic energy to internal rotation energy is 431 cm⁻¹, still considerably below the total available energy. The parity changing collision induced transition, for which the energy change is only 0.05 cm⁻¹, presents the largest cross section: \((41.6\pm1.3)\%\) of the scattered molecules arrive in the lower A-doublet state. The relatively large value of the relative cross section for the transition to \(\Omega'=1/2, J'=3/2\) and \(5/2\) \(e\) states is due to the fact that it consists of contributions from excitations to both these rotational states, probed by transitions unresolved within the laser bandwidth.

As given by Eq. (2b) the quantity \(F_{\text{out}}(\Omega'', J'', e'')\), i.e., the denominator in Eq. (1), is the same for all the final states probed, but it can differ from system to system. Therefore, for the comparison among OH–HX systems the ratios of the measured cross sections to the cross section for the transition to \(\Omega'=3/2, J'=3/2, e\) states are considered:

**TABLE II. Relative state-to-state cross sections, \(\sigma_{\text{rel}}(\%)\), for inelastic scattering of OH (\(X^2\Pi, v=0, \Omega=3/2, J=3/2, f\)) in collisions with pure HI (\(^3 \Sigma, v=0, J<4\)) at 690 cm⁻¹ collision energy.**

<table>
<thead>
<tr>
<th>Final state</th>
<th>(\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></td>
<td>41.67±1.34</td>
</tr>
<tr>
<td>5/2</td>
<td>3/2</td>
<td></td>
<td></td>
<td>4.76±0.62</td>
</tr>
<tr>
<td>7/2</td>
<td>3/2</td>
<td></td>
<td></td>
<td>1.71±0.53</td>
</tr>
<tr>
<td>9/2</td>
<td>3/2</td>
<td></td>
<td></td>
<td>0.81±0.64</td>
</tr>
<tr>
<td>1/2</td>
<td>1/2</td>
<td></td>
<td>0.32±0.45</td>
<td>0.96±0.31</td>
</tr>
<tr>
<td>3/2</td>
<td>1/2</td>
<td></td>
<td>0.11±0.37</td>
<td>1.99±0.44</td>
</tr>
<tr>
<td>5/2</td>
<td>3/2</td>
<td></td>
<td>0.25±0.42</td>
<td>0.11±0.37</td>
</tr>
<tr>
<td>7/2</td>
<td></td>
<td></td>
<td>0.03±0.63</td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\)The \(\Omega=1/2, J=3/2\) and \(5/2\), \(e\) state populations are probed by transitions which are not separated within the laser bandwidth.
FIG. 2. Ratios, \( p(\Omega', J', e') \) (%), of the absolute state-to-state cross sections and the absolute cross section for the transition to the \( \Omega'=3/2, J'=3/2, e \) state of OH (\( X^2\Pi, v=0, \Omega''=3/2, J''=3/2, f \)) in collisions with HI at 690 cm\(^{-1}\) collision energy (triangles), with HBr at 750 cm\(^{-1}\) collision energy (circles), and with HCl at 920 cm\(^{-1}\) collision energy (squares), for the transitions to the (a) \( \Omega'=3/2 \) states and (b) \( \Omega'=1/2 \) states. The error bars correspond to one standard deviation.

\[
p(\Omega', J', e') = \frac{\sigma_{rel}(\Omega', J', e')}{\sigma_{rel}(3/2, 3/2, e)} \times 100(\%).
\]  

Assuming that the product \( v_{rel,OH}n_{HIX} \) is constant over the entire detection volume the resulting ratios, \( p(\Omega', J', e') \), are the ratios of the absolute state-to-state cross sections for the transition to each probed state to the absolute cross section for the transition to the \( \Omega'=3/2, J'=3/2, e \) state. These ratios are shown graphically in Fig. 2 for the OH–HI system at 690 cm\(^{-1}\) collision energy, for the OH–HBr system at 750 cm\(^{-1}\) collision energy, and for OH–HCl at 920 cm\(^{-1}\).

**B. Steric asymmetries**

In order to orient the state selected OH molecules parallel or antiparallel to the relative velocity vector of the OH–HI system the electrostatic field is switched on between the four rods in the collision region. Either the O or the H side is turned toward the HI molecule depending on the polarity of the rods. The degree of orientation is given by the average value of the angle between the molecular axis and the axis of the external field:

\[
\langle \cos \theta \rangle_{M_J}(E) = 2 \alpha_{M_J}(E) \beta_{M_J}(E) \frac{M_J \Omega}{J(J+1)},
\]  

where \( M_J \) is the projection of the total molecular angular momentum on the external field axis and \( \alpha_{M_J} \) and \( \beta_{M_J} \) are the parity mixing coefficients. The electric field dependent wave functions corresponding to each parity of the \( J=3/2 \) \( \Lambda \)-doublet states, \( \psi_f \) and \( \psi_e \), are expressed as linear combinations of the field-free wave functions:

\[
\psi_f(E) = \alpha_{M_J}(E) |\Omega JM_J f\rangle + \beta_{M_J}(E) |\Omega JM_J e\rangle,
\]  

\[
\psi_e(E) = \alpha_{M_J}(E) |\Omega JM_J e\rangle - \beta_{M_J}(E) |\Omega JM_J f\rangle.
\]  

The 7.5 kV/cm field strength used for the orientation of the state selected \( \Omega''=3/2, J''=3/2, M_J'=3/2, f \) molecules pro-
TABLE III. Steric asymmetries, $S(\%)$, for rotationally inelastic scattering of OH ($\chi^2\Pi, v=0, \Omega=3/2, J=3/2, f$) in collisions with pure HI ($\Sigma, v=0, J<4$) at 690 cm$^{-1}$ collision energy.

<table>
<thead>
<tr>
<th>Final state</th>
<th>$\Omega$</th>
<th>$J$</th>
<th>$f$</th>
<th>$e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3/2</td>
<td>5/2</td>
<td>$-1.2\pm4.8$</td>
<td>8.2$\pm2.8$</td>
<td></td>
</tr>
<tr>
<td>7/2</td>
<td></td>
<td>$-0.5\pm8.0$</td>
<td>7.5$\pm5.9$</td>
<td></td>
</tr>
<tr>
<td>1/2</td>
<td>1/2</td>
<td>...</td>
<td>1.6$\pm6.1$</td>
<td></td>
</tr>
<tr>
<td>3/2</td>
<td></td>
<td>...</td>
<td>3.3$\pm6.7$</td>
<td></td>
</tr>
</tbody>
</table>

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

The state-to-state steric asymmetry used to quantify the effect of the OH molecules orientation on the scattering process is defined as follows:

$$S(\Omega', J', e') = 100 \times \frac{\sigma_{\text{HO-C}} - \sigma_{\text{OH-C}}}{\sigma_{\text{HO-C}} + \sigma_{\text{OH-C}}}, \quad (7)$$

where $\sigma_{\text{HO-C}}$ or $\sigma_{\text{OH-C}}$ represents the cross section for the collision induced transition from the $\Omega''=3/2, J''=3/2, f$ state to the $\Omega', J', e'$ state of the OH radical oriented with the O or H side, respectively, toward the collision partner, C. A positive steric asymmetry indicates a preference for scattering at the O side and alternatively, a H side preference corresponds to a negative value of the steric asymmetry. The results for the measured steric asymmetries corresponding to state-to-state rotationally inelastic scattering of OH by HI are presented in Table III. Figure 3 shows the graphical compari-
TABLE IV. Transitions used for the REMPI detection of the atomic halogen product of the OH+HX reactions, for X=Cl, Br, and I.

<table>
<thead>
<tr>
<th>Reaction product</th>
<th>Transition</th>
<th>Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>(1+1') REMPI</td>
<td>118.87</td>
</tr>
<tr>
<td></td>
<td>(2D_{3/2} \rightarrow 2P_{3/2})</td>
<td>120.136</td>
</tr>
<tr>
<td>Br</td>
<td>(2+1) REMPI</td>
<td>264.211</td>
</tr>
<tr>
<td></td>
<td>(2D_{3/2} \rightarrow 2P_{3/2})</td>
<td>266.697</td>
</tr>
<tr>
<td>I</td>
<td>(2+1) REMPI</td>
<td>304.025</td>
</tr>
<tr>
<td></td>
<td>(5\ell[2]<em>{j=2} \rightarrow 2P</em>{3/2})</td>
<td>142.550</td>
</tr>
</tbody>
</table>

son with the steric asymmetries measured for scattering of OH by HCl (Ref. 11) and by HBr.12

C. Reaction products

One of the highest reactivities reported for the hydroxyl radical involves the halogen hydrides. These reactions are highly exothermic:

\[ OH + HCl \rightarrow H_2O + Cl, \quad \Delta H_0^f = -5534 \text{ cm}^{-1}, \quad (8a) \]

\[ OH + HBr \rightarrow H_2O + Br, \quad \Delta H_0^f = -10992 \text{ cm}^{-1}, \quad (8b) \]

\[ OH + HI \rightarrow H_2O + I, \quad \Delta H_0^f = -16685 \text{ cm}^{-1}. \quad (8c) \]

As hydrogen atom transfer reactions they constitute a step in computational complexity from atom-diatomic to diatom-diatomic systems. According to the kinetic and photochemical data given by the IUPAC Subcommittee for Gas Kinetic Data Evaluation,20 reaction (8a) presents a thermal rate at 298 K of \((7.8 \pm 0.1) \times 10^{-13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}\), which increases with the temperature. Conversely, for reactions (8b) and (8c) the thermal rates decrease with an increase in temperature. At 298 K, rate constants of \((1.1 \pm 0.1) \times 10^{-11}\) and \((7.0 \pm 0.3) \times 10^{-11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}\), respectively, are reported.20 For the OH+HCl and OH+HBr reactions, barrier heights of around 300–900 and 0–300 \text{ cm}^{-1}, respectively, are found, whereas no barrier at all for OH+HI.

For all three systems OH \((X^2\Sigma_{3/2}, \nu=0,J=3/2,f)\) +HX we tried to observe the atomic reaction product X=Cl, Br, and I by applying \((1+1')\) or \((2+1)\) REMPI using the transitions given in Table IV. The vuv radiation was produced by the third harmonic generation in Xe or Kr of the neodymium doped yttrium aluminium garnet pumped dye laser output, operating with the dyes LD 700 or LD 750 and subsequently doubled in frequency \((\approx 6 \text{ mJ/pulse})\) or with stilbene 3 \((25 \text{ mJ/pulse})\). The UV radiation \((\approx 3 \text{ mJ/pulse} \text{ at } 266 \text{ nm} \text{ and } \approx 5 \text{ mJ/pulse} \text{ at } 305 \text{ nm})\) was obtained by frequency doubling in a Beta-Barium-Borate crystal of the dye laser output using the C 153 and SR 640 dyes. For the Br and I atoms detection of the laser was only weakly focused in order to increase the detection volume and to reduce the background atom signal due to the photodissociation of the hydride. In order to detect the ionized atoms we employed the velocity map imaging detection method, such that the products of the reaction and the photolysis could be separated by their kinetic energy. Unfortunately, summations of images up to 150 000 shots did not reveal a reaction signal thus far. Since the measurement methods were different for the inelastic and the reactive scattering, an upper limit for the cross sections for these reactive channels could not be derived.

IV. DISCUSSIONS

Relative to the amount of molecules that due to collisions with HI molecules change only the state parity, the amount of molecules rotationally excited decreases with increasing rotational quantum number and this trend is notable for all halogen hydride partners. The cross sections for the spin-orbit conserving transitions decrease faster with the rotational excitation for OH scattered by HI than by the other two halides. The cross sections for the transitions that require both spin-orbit and electronic symmetry change, i.e., to \(\Omega' = 1/2, f\) final states are zero or undetermined. For this reason the corresponding steric asymmetries were not measurable. No propensity with respect to the A-doublet parity is measured within the experimental accuracy for OH–HCl and OH–HBr, while for OH–HI at lower rotational excitations a propensity for the \(\Omega' = 3/2, f\) and \(\Omega' = 1/2, e\) states is revealed. The \(\Omega' = 3/2, f\) and \(\Omega' = 1/2, e\) states correspond to the same electronic configuration with the unpaired electronic orbital antisymmetric with respect to a reflection in the molecular rotation plane. In collisions with HI, the OH molecules exhibit a tendency to retain this configuration above changing it into the orbital configuration symmetric with respect to the reflection in the molecular rotation plane. This is in agreement with the very small cross sections mentioned above. It is expected that the intermolecular interactions based on the electric quadrupole moment and polarizability (Table I) are stronger for OH–HI than for the OH–HBr and OH–HCl systems. These interactions may differ for the two electronic configurations, resulting in such a symmetry propensity. It is notable that a reversed preference, mainly for \(\Omega' = 3/2, f\) and \(\Omega' = 1/2, e\) states has been found for the inelastic scattering of OH by N\(_2\), CO\(_2\), and CO, which have a significant negative electric quadrupole moment, and for scattering by He and Ar, which have only small polarizabilities.

Concerning the steric asymmetries, the experimental accuracy is lower for the results for OH–HI. A preference for the O-side impact is present for the parity changing transitions, i.e., \(\Omega' = 3/2, J' = 5/2\) and \(7/2, e\) final states. All the other transitions measured present very small asymmetries, similar to the results obtained for the OH–HBr oriented scattering.

Measure of the interaction strength, the depth of the global minimum of the PES decreases with the dipole moment of the halogen hydride for OH–HCl (Ref. 17) and OH–HBr.18 Besides the type and strength of the interaction, the differences in results for the OH inelastic scattering by HCl, HBr, and HI molecules may be linked to the occurrence...
of reactions, to the different temperature dependences of the reaction rate constants, and to the different vibration distributions of the H$_2$O product, as measured by Butkovskaya and Setser.\textsuperscript{13,14} The reaction dynamics found using flow measurements indicate two possible mechanisms involving either direct abstraction or addition migration of the H atom. The hydrogen atom migration mechanism requires an attack of the OH molecule on the halogen part of the encountered hydride. However, in the configurations for the transition states and the most stable hydrogen bonded complexes, as derived by \textit{ab initio} computations for OH–HCl (Ref. 17) and OH–HBr (Ref. 18) systems, the H’ side of the halogen hydride is closer to the OH molecule, the H–O–H’ bonds being very close to the stable water molecule geometry. The OH–HCl four-dimensional diabatic PESs, computed by Wormer \textit{et al.} and correlated with the twofold degenerate ‘$\Pi$’ ground state of the hydroxyl radical, reveals besides the HO–H’Cl global minimum with a well depth of 1123 cm$^{-1}$ a local minimum with an energy well of 655 cm$^{-1}$, for which the molecular configuration is very different.\textsuperscript{17} The Cl atom is approached by the hydroxyl radical forming an almost T shape OH–ClH’ complex. This minimum is attributed mainly to the dipole-quadrupole interaction, while the global minimum reflects more the dipole-dipole interaction. If the configuration of the local PES minimum is the only one having the halogen atom toward the hydroxyl radical, it is probably close to the configuration required for the H’ migration mechanism. It should be noted that from HCl to HBr and HI the permanent electric dipole moment decreases and the quadrupole moment increases (Table I) which would lead to a less deep HO–H’X minimum of the PES and relatively deeper OH–XH’ minimum. This is consistent with an increasing competition between the direct and migration reaction mechanisms for OH+H’X reactions, going from X =Cl to Br and I, according to the conclusions of Butkovskaya and Setser. Indeed, Liu \textit{et al.}\textsuperscript{18} found the HO–H’Br complex well almost two times less deep than the HO–H’Cl well and Deskevich \textit{et al.}\textsuperscript{19} found the deepest well for HO–H’F, about 4000 cm$^{-1}$, where HF has the largest dipole moment and the lowest quadrupole moment among the electric moments of HX molecules, X=F, Cl, Br, and I. It is thus possible that two complex wells are correlated to two reaction mechanisms that lead to the same products (microscopic branching\textsuperscript{5,16}) and that the branching ratios for the two channels are different for the OH+H’X systems, with X =Cl, Br, and I.

It is interesting that the configurations for the two potential wells exhibit different orientations of the molecules with respect to each other. The presence in the PES of two minima, one for a linear HO–H’X configuration and the other for a T shaped OH–XH’ configuration, which are both related to the reaction occurrence, may determine small steric asymmetries.

For the HCl case the global minimum is very deep when compared with the local one, thus the O side is presumed to be preferred for sampling the HO–H’Cl well region, yielding strong anisotropy effects. This presumption can be confirmed by the negative steric asymmetries. This would indicate smaller inelastic cross sections for collisions involving the hydroxyl radical oriented with the O side toward the HCl molecule compared to the cross sections for collisions of OH oriented with the H side toward HCl, on the account of the losses due to the reaction via the direct H atom abstraction. Such large negative steric asymmetries are observed for the spin-orbit and parity conserving transitions, $\Omega'=3/2, \ J'=5/2, \text{and } 7/2, f$, of OH molecules scattered by HCl [Fig. 3(a), left panel]. It is likely that in the OH–HCl collisions the H side oriented OH molecules, which may not undergo a path sampling a complex region of the PES, prefer to conserve their initial state spin-orbit and symmetry, $\Omega'=3/2, f$. For collisions with HBr and HI the second reaction mechanism, via the OH–XH’ complex, might become important and therefore both the H and O sides oriented molecules may be lost by reaction, resulting in smaller measured steric asymmetries. This is in good agreement with the experimental results, which show almost no steric asymmetries for the OH scattering by HBr and HI (Fig. 3).

For the symmetry changing transitions, $\Omega'=3/2, e$ [Fig. 3(a), right panel] the steric asymmetries for OH–HI are small and clearly positive. The relative state-to-state cross sections of these collision induced transitions are smaller than the cross sections for the transitions to the $\Omega'=3/2, f$ states (Table II). The effect might be ascribed to the interaction involving the HI electric quadrupole moment and polarizability. Transitions to the $\Omega'=3/2, e$ states exhibit smaller cross sections and more positive steric asymmetries than transitions to $\Omega'=3/2, f$. Thus, fewer molecules are scattered to the e states and in these collisions the O side orientation is preferred. This can be correlated to the losses by reaction via the H’ migration mechanism, in which the OH–XH’ complex and the interaction due to the quadrupole electric moment are involved, if such a reaction mechanism indeed plays a role in the OH–HI interaction.

Other possible effects on the measured steric asymmetries may be related to the occurrence of the exchange reaction, OH+H’X $\rightarrow$ OH+HX, and to the OH reorientation. The exchange reactions for the interactions of hot H atoms with H’X molecules have larger cross section and smaller barrier energy going from X=Cl, Br to I.\textsuperscript{21} Our measurements cannot give information about the branching ratio between such reaction and the translation-rotation energy transfer for the OH–H’X interactions. The decrease of measured cross sections with the rotational excitation is found to be faster for OH scattered by HI followed by HCl and HBr. If the exchange reaction takes place it may influence the results for the steric asymmetries in the sense that a certain orientation of the OH prior to the collision can be favored for the reaction, possibly the H side (negative S). Weaker measured steric asymmetries can be due to the possible reorientation of the OH molecules in the presence of the encountering polar molecule.

V. SUMMARY

State-to-state rotationally inelastic cross sections and steric asymmetries for the hydroxyl radical in collisions with hydrogen iodide have been measured in a crossed molecular beam experiment. The differences in mass, size, electric mo-
ments, and polarizability of the chlorine, bromine, and iodine hydrides are reflected in the experimental results presented. A comparison among the three molecular systems points toward rich PES landscapes that are not yet completely known. Findings from previous kinetic reports and improved calculations are used as support for a qualitative discussion of the anisotropy of the OH–HX (X=Cl, Br, and I) interaction potentials.

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