Rotational alignment of products from NOCl+Sr chemiluminescent reaction

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The chemiluminescent reactions Sr+NOCl→SrCl(A,B)+NO are studied under the single collision conditions in a beam-gas arrangement. The product rotational alignment \(P_z(\mathbf{J} \cdot \mathbf{k})\) = -0.40 ± 0.05 for SrCl(B) is obtained from Sr+NOCl chemiluminescent reactions. In addition, the electronic state branching ratio and the product vibrational state distribution have been roughly estimated by simulating the chemiluminescent spectra of SrCl. Quasiclassical trajectory (QCT) calculations for the Sr+NOCl reaction as a three-body system have been carried out. The calculated results agree well with the experimental ones. © 1998 American Institute of Physics.

I. INTRODUCTION

Theoretical and experimental interest in vector correlation in the reaction processes

\[ A + BC \rightarrow AB + C \]  

has increased significantly in recent decades. Only by understanding the scalar and vector properties together, as well as possible correlation among them, can the fullest pictures of the scattering dynamics emerge. In order to investigate the vector correlation in the scattering process, not only the magnitudes, but also well defined directions of the vectors during the scattering process should be determined. The study of orientation and alignment can give the correlation of angular momentum vectors in a reaction. Several experimental methods, such as polarization-resolved chemiluminescence, polarized laser-induced fluorescence, electric deflection methods, REMPI, etc., have been developed to study orientation and alignment in chemical reaction under molecular-beam and bulb conditions. Among them, the method of chemiluminescence combined with molecular beams is the simplest and easiest, although this type of method is limited to the reactions giving products chemiluminescence.

At the same time, the theoretical study of the orientation and alignment of angular momentum vectors in the reaction plays an important role as well. Hijazi and Polanyi used QCT methods on two potential energy surfaces, one attractive and one repulsive, to investigate the effects of different mass combinations of reactants on the distribution of angles between product rotational angular momentum and reactant relative velocity and the role of reactant orbital angular momentum in determining \(J'\). Recently, Han et al. reported the product rotational alignment of several mass combination reactions as a function of collision energies on attractive and repulsive potential surfaces. In another paper of Li et al., the impulse model indicated that either low repulsive energies or large orbital angular momentum of reactants or \(H' + HL\) mass combination might lead to a strong alignment of the product rotation.

Reactions between alkaline earth metal atoms and halogenated hydrocarbon molecules have been extensively studied. Stolte and co-workers summarized the reactions between alkaline earth metal atoms and halogenated methane. The crossed beam reactive scattering of Ca,Sr,Ba+CH_3I was first studied by Lin et al. The products of these reactions were found to scatter predominantly backward in the center-of-mass frame with substantial recoil energy, indicating that the reactions proceed via an impulsive mechanism. Recently, Han et al. reported nascent BaBr product internal state distributions of the reactions between Ba(\(^1S_0\)) and C_\(n\)H_\(2n+1\)Br (\(n=1,2,3,4,5\)). It has been found that the BaBr product vibrational excitation slightly increases with the increment of the number of the carbon atoms of the alkyl radical \(R\) in the BaBr series of CH_3Br, C_2H_5Br, n-C_3H_7Br, n-C_4H_9Br, whereas the BaBr product vibrational excitation for the reactions Ba+(\(n,i,s,t\))-C_\(n\)H_\(2n\)Br is almost identical. Quasiclassical trajectory calculations based on the empirical LEPS potential energy surfaces and simple dynamical model analysis show that the differences of the product vibrational state distributions are mainly caused by those of the mass factors among these reactions.

In addition, a large number of studies have been reported on the reactions of electronically excited atoms. The reactions of Ca* with CH_3F, CH_3Cl, and CH_3Br (Refs. 36–38) and our recent study of reactions Sr* with CH_3I, C_2H_5I (Ref. 39) are examples which are the visible chemiluminescence experiments. The other reactions of Ba* with CH_3Cl and CF_3Cl (Ref. 40) and of Ca* with CH_3Cl_2 and CHCl_3 (Ref. 41) are other examples which are the LIF experiments. Recently, the chemiluminescence of CaI* was studied for the reactions of orbital aligned Ca(\(^1P_1\)) with CH_3I. In a previous paper, preliminary results of the product rotational alignment for the reactions Ca+NOCl together with the discussion of influence of reaction potential energy surfaces on the reactions were reported. The product rota-
tional alignment for CaCl($B$) is $\langle P_2(\hat{J} \cdot \hat{k}) \rangle = -0.35 \pm 0.04$. The strong product alignment for the reaction is attributed to an attractive potential surface. In this paper, the Sr$^+$NOCl$\rightarrow$SrCl($A^2\Pi_{1/2,3/2}$, $B^2\Sigma^+$) + NO reaction has been studied by measuring their chemiluminescence. The rotational alignment of the product SrCl($B^2\Sigma^+$) was probed experimentally. In addition, the electronic state branching ratio and the product vibrational state population have been roughly estimated by simulating the chemiluminescent spectrum of SrCl.

II. THEORY

The theory about rotational alignment in chemical reactions and the method for obtaining the rotational alignment of a product in a chemiluminescent reaction from the polarizational degree of chemiluminescence are based on Refs. 3 and 2, and were summarized in our previous paper. Briefly, $L$ and $L'$ denote the orbital angular momenta of the reactant and product; $J$ and $J'$ denote the rotational momenta of the reactant and product, respectively. $Z$ is the symmetrical axis in the experimental configuration. Then a symmetrical distribution of the rotational angular momentum of the product, $f(\hat{J} \cdot \hat{Z})$ can be expressed as a Legendre expansion

$$f(\hat{J} \cdot \hat{Z}) = \sum_{\ell} a_{\ell} P_{\ell}(\hat{J} \cdot \hat{Z}),$$

(2)

in which the superscript $^\wedge$ denotes unit vectors, the coefficients $a_1$ and $a_2$, which are proportional to $\langle P_1(\hat{J} \cdot \hat{Z}) \rangle$ and $\langle P_2(\hat{J} \cdot \hat{Z}) \rangle$, are used to describe the orientation and alignment of the products, respectively. (The angular brackets denote the average of the items.) The degree of polarization of chemiluminescence $P$ can be related to the distribution of angular momentum vectors of the emitting molecule

$$P(P, R \text{ line}) = -3 \langle P_2(\hat{J} \cdot \hat{Z}) \rangle / (4 - \langle P_2(\hat{J} \cdot \hat{Z}) \rangle),$$

(3)

$$P(Q \text{ line}) = 3 \langle P_2(\hat{J} \cdot \hat{Z}) \rangle / (2 + \langle P_2(\hat{J} \cdot \hat{Z}) \rangle),$$

(4)

where

$$P = (I_1 - I_2) / (I_1 + I_2).$$

(5)

For a parallel-type transition, such as SrCl($B^2\Sigma^+$) → SrCl($A^2\Pi_{1/2,3/2}$), only $P$ and $R$ rotational branches are present, and $\langle P_2(\hat{J} \cdot \hat{Z}) \rangle$ can be calculated by using expression (3). For a perpendicular-type transition, the spectrum may contain either $P$, $R$ branches or a $Q$ branch. $\langle P_2(\hat{J} \cdot \hat{Z}) \rangle$ should be calculated by using both expression (3) and expression (4) for different rotational branches, respectively.

The rotational alignment in the laboratory frame should be converted into the center of mass frame by using the expression

$$\langle P_2(\hat{J} \cdot \hat{k}) \rangle = \langle P_2(\hat{J} \cdot \hat{Z}) \rangle / \langle P_2(\hat{k} \cdot \hat{Z}) \rangle$$

(6)

for a beam-gas reaction. $\langle P_2(\hat{k} \cdot \hat{Z}) \rangle$ is given by Monte Carlo calculation.

The limitation of $\langle P_2(\hat{J} \cdot \hat{k}) \rangle$ is between 0.5 to 1.0. A strong rotational alignment of the reaction product corresponding to a value of $\langle P_2(\hat{J} \cdot \hat{k}) \rangle$ is close to 0.5, such as the $H + H'$ → $HH' + L$ reaction, while a random direction distribution of rotational angular momentum corresponding to a value of $\langle P_2(\hat{J} \cdot \hat{k}) \rangle$ is close to zero.

III. EXPERIMENT

The experiments were carried out in a beam-gas apparatus. The beam-gas apparatus was described in detail elsewhere. The experiments were also described in our previous paper. Briefly, Sr metal is heated to 970 K in a stainless steel crucible heated by an electrothermal wire. The beam of metal atoms effuses to the main chamber which is filled with the reaction gas. The pressure of the reactant gas is lower than 0.02 Pa, in order to satisfy single collision conditions.

The chemiluminescence of the nascent product SrCl($A$) and SrCl($B$) is collected by a lens with 15 cm focal length positioned at right angles to the metal beam. A film polarizer is placed in front of a 1 m monochromator. A photomultiplier (RCA C31034) is placed behind the monochromator to detect both perpendicular and parallel components of the chemiluminescence. The output of the PMT is sent to a lock-in amplifier. The signal is collected by PC. The response of the optical system, including the monochromator, to the polarized light has been carefully calibrated.

IV. RESULTS AND DISCUSSIONS

A. Vibrational distribution and branching ratio

Figure 1(a) shows the product SrCl$^+$ chemiluminescent spectrum for the Sr$^+$NOCl$→$SrCl$^+$ + NO reaction. The spectra of $A^2\Pi_{1/2,3/2}$ → $X^2\Sigma^+$ and $B^2\Sigma^+$ → $X^2\Sigma^+$ emissions are overlapped together. Usually, it is difficult to estimate the $A$, $B$ state branching ratio and other information for the SrCl. In
In order to determine the $A$, $B$ state branching ratio and vibrational distributions of SrCl, a spectrum simulation was performed. Figure 1(b) shows the simulated spectrum of SrCl$^*$. In the simulation, the spectroscopic constants are taken from Ref. 44. The vibrational population distributions of the emitting states are proposed to adjust both the relative intensities of vibrational sequences and electronic branching ratio. By comparing the simulated spectrum with the observed spectrum, the vibrational population and electronic branching ratio are estimated. Both the relative intensities of vibrational sequences and electronic branching ratio are sensitive to the vibrational population in simulation, but are not sensitive to rotational population. The rotational population in simulation is taken as Boltzmann population and the rotational temperature is 1000 K. The thermal rotational distribution gave a satisfactory simulation result in the line shape and the relative intensity of different vibrational sequences.

The simulated vibrational distributions of $A$ $^3\Pi_{1/2}$, $A$ $^3\Pi_{3/2}$, and $B$ $^2\Sigma$ states are shown in Fig. 2. The populated vibrational quantum numbers are in the range of $v = 2-25$, 0–14, and 0–11 for $A$ $^3\Pi_{1/2}$, $A$ $^3\Pi_{3/2}$, and $B$ $^2\Sigma$ states, respectively. The maximum vibrational distribution are at $v = 10$, 5, and 4 for $A$ $^3\Pi_{1/2}$, $A$ $^3\Pi_{3/2}$, and $B$ $^2\Sigma$ states, respectively. For the $A$ $^3\Pi_{1/2}$ electronic state of the product SrCl, the higher vibrational levels are populated than those of the $A$ $^3\Pi_{3/2}$ and $B$ $^2\Sigma$ state, because the energy level for the $A$ $^3\Pi_{1/2}$ state is lower than that of $A$ $^3\Pi_{3/2}$ and $B$ $^2\Sigma$ states. This is similar to most other reactions. 31,39

The branching ratio for $A$ and $B$ excited states is obtained to be 2.35:1. This result is close to that of the Sr($^3P_J$)+CH$_3$CH$_2$I reaction system, 2.32:1, 39 and that of Ca($^1D_2$,$^3P_J$)+RI (R=CH$_3$,C$_2$H$_5$, and n-C$_6$H$_{13}$) reaction systems, 2.41, 45 but is somewhat smaller than that of the reaction Ca+NOCl. 2.57:1 (Ref. 43) or 2.85:1. 46

According to statistical theory, the corresponding statistical or ‘prior’ branching ratios are given by

$$P_\alpha = g_\alpha \rho_\alpha(E_a) / \sum_\alpha g_\alpha \rho_\alpha(E_a),$$

where $\alpha$ denotes individual states of the product; $g_\alpha$ is the statistical weight factor of each electronic state; $\rho_\alpha(E_a)$ is the quantum phase space density of the corresponding states; $E_a$ is the available energy for the $\alpha$ excited state. Taking the NO molecule as a vibrating-rotor, we obtained the theoretical prediction of the branching ratio for the product SrCl in the $A$ and $B$ states is 2.72:1. However, the experimental data on the distribution of vibrational energy of SrCl at the electronic states may provide additional constraints on the electronic reaction channels, therefore it may cause a deviation in branching ratio from statistical behavior. If the deviation is taken into account, the ‘prior’ branching ratio can be expressed in terms of an ‘entropy deficiency’ for electronic product channel $\alpha$ (Refs. 47 and 48).

By using the ‘linear surprisal’ model, 38 the branching ratio into the product channel $\alpha$ is given by 47,48

$$P_\alpha = P_\alpha^0 \exp(-\Delta S_\alpha/R) / \sum_\alpha P_\alpha^0 \exp(-\Delta S_\alpha/R),$$

where the ‘prior’ branching ratios $P_\alpha^0$ are given by expression (7), $\Delta S_\alpha$ is the ‘entropy deficiency.’ Assuming that the vibrational and rotational surprisals of the NO molecule and the rotational surprisal of SrCl are zero, the calculation gives a result for the branching ratio of SrCl($B$):SrCl($A$) = 1:2.54.

If the product NO molecule is assumed as only a linear rotor, the predictive results of the branching ratio for the product SrCl in $A$ and $B$ electronic states is 2.35:1, which is in good agreement with the experimental result. It may come to a conclusion that the reactions have additional constraints besides the vibrational motion of the SrCl molecule. In Ref. 39, the predictive results by statistical theory is in good agreement with the experimental results, only when the alkyls in the iodine alkyl reactants were taken as particles. This may also be caused by the existence of dynamical constraints in the reactions.

Another explanation for the deviation of statistical prediction of the branching ratio from the experimental result may be the different features in the potential surfaces for producing the two different states. The forming $B$ $^2\Sigma$ state SrCl molecule may be easier than the $A$ $^3\Pi$ state.

B. Rotational alignment of SrCl($B$)

The degree of polarization of the SrCl($B$ $^2\Sigma^+ + X$ $^2\Sigma^+$) transition is obtained by detecting the parallel and perpendicularly polarized components of the chemiluminescence referring to the direction of the beam. For the $\Sigma^-$-$\Sigma$ transition, only $P$ and $R$ branches can be observed.

The $\langle P_2(\hat{J}\cdot\hat{k}) \rangle$ of the product SrCl($B$) for the Sr+CINO reaction system approaches −0.5. As mentioned above, typically, the rotational angular momentum of the product for a large cross section $H^+ + HL \rightarrow H^+H + L$ reaction will be strongly aligned, but the mass combination of the Sr+CINO reaction is far from the $H^+ + HL$ mass combination. Why is the product SrCl($B$) rotation strongly aligned?
TABLE I. Summary of product alignment for the experiments.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Method</th>
<th>Product</th>
<th>$\langle P_z(J'\cdot k) \rangle$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr$^1(P_j$ + CH$_3$I$^*$</td>
<td>Chemiluminescence</td>
<td>SrI$^*$</td>
<td>$-0.48 \pm 0.02$</td>
</tr>
<tr>
<td>Sr$^1(P_j$ + C$_2$H$_5$I$^*$</td>
<td>Chemiluminescence</td>
<td>SrI$^*$</td>
<td>$-0.19 \pm 0.02$</td>
</tr>
<tr>
<td>Sr$^2(S_p$ + CH$_3$Br$^*$</td>
<td>Polarized LIF</td>
<td>SrBr$^*$</td>
<td>$-0.34 \pm 0.04$</td>
</tr>
<tr>
<td>Sr$^2(S_p$ + C$_2$H$_5$Br$^*$</td>
<td>Polarized LIF</td>
<td>SrBr$^*$</td>
<td>$-0.24 \pm 0.04$</td>
</tr>
<tr>
<td>Sr$^2(S_p$ + C$_3$H$_6$Br$^*$</td>
<td>Polarized LIF</td>
<td>SrBr$^*$</td>
<td>$-0.24 \pm 0.04$</td>
</tr>
<tr>
<td>Ca$^1(P_j$ + CH$_3$I$^*$</td>
<td>Chemiluminescence</td>
<td>CaI$^*$</td>
<td>$-0.20 \pm 0.02$</td>
</tr>
<tr>
<td>Ca$^1(P_j$ + C$_2$H$_5$I$^*$</td>
<td>Chemiluminescence</td>
<td>CaI$^*$</td>
<td>$-0.13 \pm 0.02$</td>
</tr>
<tr>
<td>Ca$^2(1P_j$ + NOCl$^*$</td>
<td>Chemiluminescence</td>
<td>CaNO$^*$</td>
<td>$-0.35 \pm 0.04$</td>
</tr>
<tr>
<td>Sr + NOCl$^*$</td>
<td>Chemiluminescence</td>
<td>SrCl$^*$</td>
<td>$-0.40 \pm 0.05$</td>
</tr>
</tbody>
</table>

$^a$From Ref. 39.  $^b$From Ref. 18.  $^c$From Ref. 42.  $^d$From Ref. 43.  $^e$This work.

We attribute the strong rotational alignment to the attractive potential. According to theoretical predictions of Han et al.,$^{30}$ for an attractive potential surface, the rotational alignment increases with the increment of collisional energies for a light light–light (or heavy heavy–heavy) mass combination. At the higher collisional energies, the orbital angular momentum of the reactants is large, while the rotational excitation comes from both the orbital angular momentum of the reactants and the repulsion between the products. The contribution of the repulsion of the direction of the rotational angular momentum of the products may differ from that of the orbital momentum of the reactants. The repulsive energy gives a distribution of rotational angular momentum vectors of the products which is less anisotropic. Clearly, the higher the collisional energies are, the stronger the rotational alignment of the products will be. In the strong attractive surface for the Sr + NOCl reaction, the product rotation may be strongly aligned even at very low collisional energies.

Comparing the results of the Ca + NOCl reaction,$^{43}$ we found the rotational alignment of SrCl(B) to be stronger than that of CaCl(B). This may be attributed to a mass effect, i.e., the Sr atom is heavier than the Ca atom and thus the rotational alignment of the product SrCl(B) is stronger than that of CaCl(B).$^{32}$ The mass effect was observed in many other reactions.$^{18,39,42}$ For the reactions Ca$^1(1P_j$ + CH$_3$I, CH$_3$CH$_2$I, the rotational alignment parameters of the product CaI(B) are $-0.2$ and $-0.13$.$^{42}$ For the reactions Sr + CH$_3$Br, C$_2$H$_5$Br, and C$_3$H$_6$Br, $\langle P_z(J'\cdot k) \rangle$ are $-0.34$, $-0.24$, $-0.14$, respectively.$^{18}$ For the reactions Sr$^1(1P_j$ + CH$_3$I, CH$_3$CH$_2$I reactions, the mass effect are more significant, i.e., $\langle P_z(J'\cdot k) \rangle$ are $-0.48$ and $-0.20$, respectively.$^{39}$ A summary of the results is listed in Table I.

C. Quasiclassical trajectory calculation

An extended LEPS potential surface for the Sr + NOCl → SrCl(B) + NO is constructed using parameters listed in Table II. A contour plot of this LEPS potential surface is given in Fig. 3. The minimum energy reaction path is shown by a dashed line, along which, the potential energy decreases monotonically from the entrance ($R_{Sr(NOCl)} = \infty$,

corresponding to reactants) to the exit ($R_{NO,SrCl} = \infty$, corresponding to products). 50 000 trajectories were sampled at a collision energy of 1.75 kcal/mol which is an average collision energy in the experiments. The QCT calculated result of $\langle P_z(J'\cdot k) \rangle = -0.40$ was obtained, which was in agreement with the experimental one.

The calculated results for the vibrational distribution is also close to the experimental ones. The average vibrational quantum number is about 5 in the QCT calculation, while the vibrational level of the maximum population is $v = 4$ in experiments. Figure 4 shows the comparison of the vibrational distribution of SrCl(B) between experiment and QCT calculation. The QCT calculation result shows a cutoff distribution at the vibration quantum number $v \cong 7$. This is caused by the fact that the collisional energy is strictly limited to 1.75 kcal/mol in the QCT calculation, while in experiments, the collisional energy follows the Boltzmann distribution. The higher vibrational distribution should correlate to the higher collisional energy in experiments.

V. CONCLUSIONS

Experimental investigations of product rotational alignments for the beam-gas chemiluminescence reaction Sr + NOCl → SrCl(A, B) + NO were carried out. The rotational alignments for the product SrCl(B) is strong, even though the mass combination for these reaction systems are
far away from the typical $H' + HL \rightarrow H' + L + H$ reaction. The strong rotational alignment is attributed to the attractive PES of the reactions.

The branching ratio of products $\text{SrCl}(B) : \text{SrCl}(A) = 1 : 2.35$ was experimentally determined for the reactions $\text{Sr} + \text{NOCl} \rightarrow \text{SrCl}(A, B) + \text{NO}$. The theoretical results are in good agreement with experimental ones when the vibrational or rotational excitation of NO is considered. The QCT calculation on the extended LEPS surface for producing $\text{SrCl}(B)$ was carried out. The calculated result for rotational alignment of products coincides well with the experimental one.

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