**Effects of reagent rotational excitation on the stereodynamics of the Ca+HCl→CaCl+H reaction**

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**Abstract**

The effects of HCl rotational excited states on the stereodynamics of the Ca+HCl reaction are explored based on quasi-classical trajectory (QCT) theory with potential energy surface (PES) [Verbockhave et al., J. Chem. Phys. 2005,122,204307]. Vibrational level *v*=0 and rotational level *j*=0-3 are considered. The polarization-dependent generalized differential cross sections (PDDCSs) and alignments of the product rotational angular momentum are used to demonstrate the stereodynamics effects. The rotational quantum number has a considerable influence on the distribution of vector correlation, including alignment, orientation, and PDDCSs. The product molecules are strongly forward and backward scattering and weakly sideway scattering because the reactant molecule HCl is in the rotational ground state and the lower rotational excited states. Strongly forward scattering is observed while the reactant is in high rotational excited states.

**KEYWORDS:** rotation of reactant molecule, vector correlation, stereodynamics, quasi-classical trajectory

**1** **|** **INTRODUCTION**

With the rapid development of reaction dynamics for computing product angular momentum polarization, studies on stereodynamics have been predicted to provide valuable information in understanding elementary reactions. A number of quasi-classical trajectory (QCT),time-independent quantum dynamics, time-dependent wave packet calculations, and density functional theory(DFT)calculations have been carried out to explore novel reaction.[1-12]

As a typical reaction of the “harpoonlike” model mechanism,[13] the Ca+HCl reaction that involves an alkali-earth atom and a hydrogen halide has been considered to analyze the influence of the initial state of the reactants on the final state distribution. The reaction M+HX→MX+H (M=Be, Mg, Ca, Sr, Ba; X=F, Cl, Br, I) shows interesting dynamical features, and many studies of this reaction family have been conducted theoretically and experimentally.[14-34] From an experimental point of view, research on the reaction dynamics of this system applied photon excitation of the Ca atom in the Ca(1S)–HCl van der Waals complex. However, the CaCl product was initially not detected in its electronic ground state[35-37] because its detection is particularly difficult. Visticot et al.[38] detected the Ca–HCl complex by observing the fluorescence of the CaCl molecule in a supersonic beam/laser-ablation experiment. In the theoretical aspect, Verbockhaven et al.[39] reported a new *ab initio* PES computed using a coupled-cluster method with single and double excitations and perturbative triples [CCSD(T)] and multi-reference configuration-interaction (MRCI) wave functions; this PES was reliable given the agreement of the quantum-dynamics calculation and the new surface with the experimental data for describing the full reaction from Ca+HCl reactants to CaCl+H products. Sanz et al.[40] performed quantum reactive-scattering calculations at the collision energy range of 0.2–1.0 eV; the reliability of the PES was confirmed by comparing the computational results with recent experimental values.

Previous studies on the Ca+HCl reaction mainly focus on scalar properties, such as rate constant, cross-section, and product population distribution. However, reports about the chemical reaction stereodynamics are few. Wang et al.[41-43] studied the vector properties of the products and investigated the variation in the rotational alignment for the Ca+HCl reaction by QCT calculations on PES developed by Verbockhaven et al.[39]; they found that the effects of isotopy and reagent vibration play an important role in the stereodynamics of the Ca+HCl reaction and its isotope reactions. However, the effects of collision energy on vector properties, including alignment, orientation, and polarization-dependent generalized differential cross sections (PDDCSs), are not obvious. To understand the scattering dynamics, we performed systematical calculations on the stereodynamics of the Ca+HCl reaction for determining the influence of the HCl rotational exited states on the reaction.

**2** **|** **Theory and computation details**

2.1 Rotational polarization of product

The computational formulae of the rotational polarization of the product can be found elsewhere[44-48]; in this work, we will only present the definitions of the vectors briefly. In the center-of-mass (CM) frame, we choose the center-of-mass (CM) frame shown in Fig. 1 to express the degree of the polarization of product rotational angular momentum***j′***. The reagent relative velocity vector ***k*** is parallel to the *z*-axis, and the*x-z*plane is the scattering plane containing the initial and final relative velocity vectors,***k*** and ***k′***.  is the angle between ***k*** and ***k′***.  and  are the polar and azimuthal angles of the final rotational angular momentum ***j′***, respectively*.*

The distribution function  describing the ***k****-****j′*** correlation can be expanded in a series of Legendre polynomials. The expanding coefficients are called orientation (*k* is odd) or alignment (*k* is even) parameters. The dihedral angle distribution function  describing ***k****-****k′****-****j′***correlation can be expanded in the Fourier series. , , and are expanded up to *k*=18, 24, 7, respectively, showing good convergence.

The fully correlated CM angular distribution is written as

. (1)

where is a generalized polarization-dependent differential cross-section (PDDCS). Many photon-initiated bimolecular reaction experiments are sensitive to only those polarization moments with *k* = 0 and ***k*** = 2. In this paper, we only calculate , , ,.

**2.2 Quasi-classical trajectory calculations**

The quasi-classical trajectory (QCT) program previously reported is used to evaluate stereodynamic properties.[41-45，48-51] The classical Hamiltonians are numerically integrated with three dimensions; the accuracy of which is verified by checking the conservation of total energy and the total angular momentum for every trajectory. A well-known drawback of QCT is its inability to properly treat quantum-mechanical effects, such as zero-point-energy problem, resonance, tunneling, and non-adiabatic transitions. Many strategies have been proposed to approximate the zero-point energy, but no satisfactory procedure has been developed. Here, a passive method of discarding all reactive trajectory-forming products with total vibrational energy lower than the total harmonic zero-point energy of the products is employed. Therefore, the QCT treatment of the reactions is accurate.

In the calculations, batches of 20,000 trajectories are run for each reaction and the integration step size of 0.1 fs is chosen. The collision energy is 0.8 eV for the title reactions. The accuracy of the numerical integration is verified by checking the conservation of the total energy and total angular momentum for every trajectory. The vibrational and rotational levels of the reactant molecules are taken as *j*=0, 1, 2, 3 and *v* =0, respectively. The trajectories start at an initial distance of 30.0 Å between the Ca atom and the center of mass of HCl. The impact parameter *bmax* values for the three reactions of Ca+HCl (*v*=0, *j*=0~3) on PES are 2.0/2.0/1.9/1.8 Å, respectively.

3 **|** **RESULTS AND DISCUSSION**

Fig. 2 shows the calculated distribution of the product from the reaction Ca+HCl(*v*=0,*j*=0-3) at a collision energy of 0.8 eV. The distribution  represents the ***k-j′*** correlation. The peak of the  distributions is at =90° and symmetric with regard to 90°; this finding demonstrates that the product rotational angular momentum vector ***j′*** is strongly aligned along the direction perpendicular to the relative velocity direction***k****.* The excitation of the initial HCl rotation has an obvious effect on stereodynamics. The peaks of the distribution of the reaction become narrow and high when the HCl molecule rotation states are excited from *j*=0 to *j*=1, implying that the product rotational alignment becomes strong; however, the peaks of the distribution of the reaction broaden and decrease with the reagent rotational quantum number increasing from *j* =1 to *j*=3, implying weakened product rotational alignment. The strongest rotational alignment effect appears first in the exciting rotation states. This phenomenon may be explained from the expectation values of, which are -0.495977, -0.496644, -0.477073, and -0.45373. <> is important because ***j****′* is preferentially polarized and perpendicular to the reagent relative velocity when the values are close to -0.5. The calculated values of  are consistent with the distributions of , verifying the reliability of the calculated results.

The dihedral angle distributions of the ***k*-*k′-j′*** correlation are compared in Fig. 3. Based on calculations at three levels of collision energies, similar features appear. The distributions of  tend to be asymmetric at approximately , reflecting the strong polarization of angular momentum for the three reactions. For each reaction, the peak at  is higher than that at , revealing that the rotational angular momentum vector of the CaCl product is not only aligned to the y-axis but also oriented toward the negative –y-direction. With increasing reagent rotational quantum number, the peaks decrease at , indicating that the orientation along the negative direction of the y-axis weakens with increasing *j*. According to a previous theoretical study[50, 51] on the molecular reaction *A+BC→AB+C*, the angular momentum of the product molecule CaCl can be written as

, (2)

, (3)

, (4)

where ***L*** and ***j*** are the reactant orbital and rotational angular momentum, respectively; is the reduced mass of the HCl molecule; ***ER*** is the repulsive energy; and ,  are unit vectors, where Cl indicates Caand Cl reflects H, respectively. During chemical bond forming and breaking for the Ca +HCl reaction, the term  in the equation is symmetric, while the term  shows a preferential direction because of the effect of repulsive energy, leading to the orientation of the CaCl product.

To obtain detailed information on the reaction dynamics, we also plot the distributions of  in Fig. 4. All  have a distinct peak at and, which are in good agreement with the distributions of  and . Furthermore, the distributions of  indicate that the products are preferentially polarized perpendicular to the scattering plane. The products of the reaction are mainly left-handed rotating in planes parallel to the scattering plane.

PDDCSs describe the ***k-k′-j′*** correlation and the scattering direction of the product molecule. The results of the reactions are shown in Fig. 5. The PDDCS , which is simply the differential cross-section (DCS), only describes the ***k-k′*** correlation or the scattering direction of the product and is not associated with the orientation and alignment of the product rotational angular momentum vector ***j′*** (Fig. 5a). Compared with the rotational ground state, the DCS is not affected by the low rotational quantum number reactants (*j*=0, 1, 2) but closely related to the high rotational quantum number of reactants (*j=* 3). Distinct scattering direction shifts in the range of *j*=0-3. The CaCl product molecules are strongly forward, backward scattering, and weakly sideway scattering for the Ca+HCl (*v*=0, *j*=0,1,2) reaction, whereas the reaction Ca+HCl (*v*=0，*j*=3) is governed by strong forward and sideways scattering. Thus, the tendency of forward scattering is enhanced with increasing rotational quantum number of the reagent. The PDDCS  is the expected value of the second Legendre moment of . The curves show the opposite trend to that of , indicating that ***j′*** is strongly aligned perpendicular to ***k***. The trend is obvious when =180°, showing the preferential polarization along the direction perpendicular to ***k***at this angle. The value of  is negative for a majority of all scattering angles, indicating the remarkable preference of the product alignment along the *y*-axis. The product displays strong polarization at approximately 38° and 142°. In the PDDCS , which is related to, the polarization of the product is enhanced in the range of *j*=0-3. The ***j****′* of CaCl shows a different distribution when the reagent molecule rotates in a different state, thereby implying the effect of reagent rotation.

1. **CONCLUSIONS**

The effects of the HCl rotational excited states on the stereodynamics of the molecular reaction Ca + HCl(*v*=0, *j*=0-3) are demonstrated by QCT. The rotational quantum number has a considerable effect on vector correlations, including alignment, orientation, and PDDCSs. The first rotational excited state plays the strongest alignment effect of the products, and the orientation effect becomes weak with increasing *j*. The rotational angular momentum vector ***j***′ of the product molecule CaCl is not only aligned but also oriented along the negative direction of the *y*-axis. CaCl shows strong forward and backward scattering and weakly sideway scattering because the reactant molecule HCl is in the rotational ground state and the low rotational excited states. However, strong forward scattering occurs when the reactant is in high rotational excited states. Furthermore, PDDCSs are influenced by the rotational excitation of the reactant. Hence, the vector properties of the reaction are affected by the rotational excited states of the reactant molecule HCl. These findings could provide helpful information to understand the microscopic mechanism of the molecular reaction Ca+HCl→CaCl+H.

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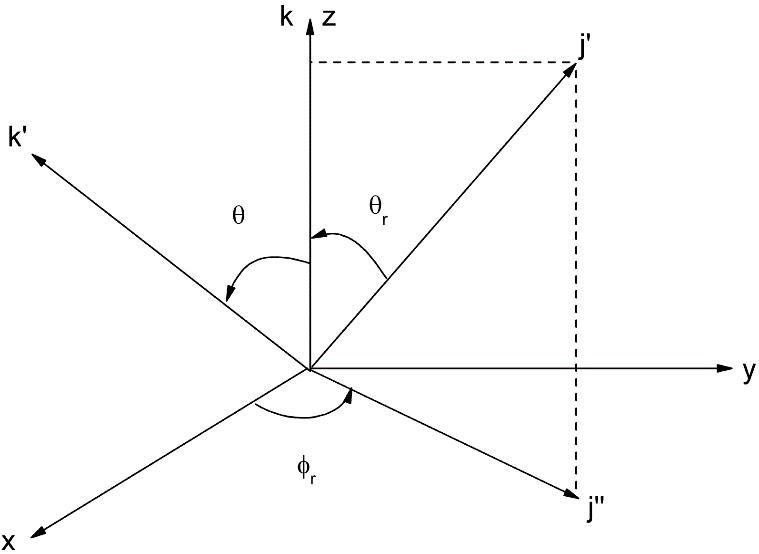
**FIGURE CAPTIONS**

**FIGURE 1.** The center-of-mass coordinate system to describe the ,  and  correlations.

**FIGURE 2.** The angular distribution of  reflecting the ***k-j*′** correlation is shown for the four reactions.

**FIGURE 3.** The angular distribution of  with respect to the ***k-k*′** plan**e.**

**FIGURE 4.** Polar plots of distribution averaged over all scattering angles.



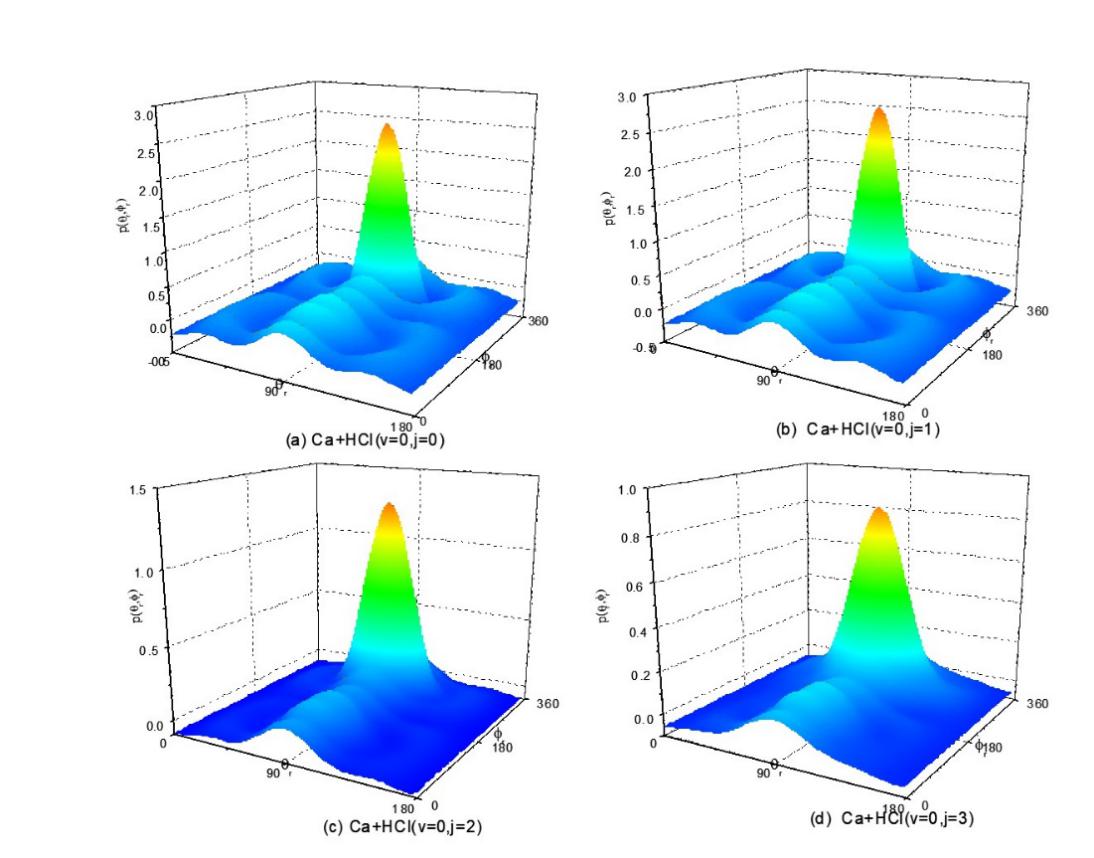
**FIGURE 1.**  The center-of-mass coordinate system to describe the ,  and  correlations.



**FIGURE 2.** The angular distribution of  reflecting the ***k-j*′** correlation is shown for the four reactions. Solid line indicates Ca+HCl(*v*=0,*j*=0); dashed line indicates Ca+HCl(*v*=0*,j*=1); dotted line indicates Ca+HCl(*v*=0,*j*=2)；dash dotted line indicates Ca+HCl(*v*=0,*j*=3)



**FIGURE 3.** The angular distribution of  with respect to the ***k-k*′** plan**e.** Solid line indicates Ca+HCl(*v*=0,*j*=0); dashed line indicates Ca+HCl(*v*=0,*j*=1); dotted line indicates Ca+HCl(*v*=0,*j*=2)；dash dotted line indicates Ca+HCl(*v*=0*,j*=3).



**FIGURE 4.** Polar plots of distribution averaged over all scattering angles. (a), (c), (b)and (d) correspond to Ca+HCl (*v*=0, *j*=0-3), respectively.



**FIGURE 5.** (a) shows the PDDCS with .Panels(b–d)depict the PDDCSs with  respectively.

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