**Stereodynamics of the Ca+HCl→CaCl+H reaction imposed by the reagent rotational-excited states**

**Li-Zhi Wang, Chuan-Lu Yang[[1]](#footnote-1)\***

*School of Physics and Optoelectronic Engineering, Ludong University, Yantai 26425, the People’s Republic of China*

**Abstract**

The influences of the initial states of HCl on the stereodynamics properties of the Ca+HCl reaction are investigated by utilizing the method based on the quasi-classical trajectory (QCT) theory and the analytical potential energy surface (APES). The orientation and alignment behaviors for the rotational angular momentum of the product, along with the generalized differential cross-section (PDDCS) dependent polarization, are employed to explore the stereodynamics properties. The initial rotational states of the HCl molecule impose a remarkable affection on the vector correlation distributions, regardless of the orientation, alignment, or PDDCS. The obvious forward or backward scattering, as well as the weak sideway scattering phenomena, are found for the different initial rotational states of the HCl molecule. The initial higher rotational-excited state of *j*=3 results in more obvious stereodynamics effects.

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

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

The investigations on the molecular reaction stereodynamics properties, such as the product angular momentum polarization, has been providing much helpful information for understanding elementary chemical reaction. Many theoretical investigations on the basis of the quasi-classical trajectory (QCT), time-dependent wave packet or quantum dynamics calculation, and density functional theory(DFT) have been carried out to explore novel reactions.[1-12]

The Ca+HCl reaction is a typical reaction with the “harpoon-like” model mechanism,[13] in which the hydrogen halide molecule and the alkali-earth atom are used to examine the impact of the reactant’s initial vibrational or rotational states on the angular momentum distribution of the final state of the product molecule. The M+HY→MY+H reactions are believed to have interesting dynamical features(here M represents Be, Mg, Ca, Sr, Ba, while Y stands for F, Cl, Br, I, respectively). Therefore, many theoretical and experimental investigations have been conducted for the reaction family.[14-34] From an experimental point of view, the reaction dynamics of the Ca+HCl reaction can be realized with the excited van der Waals complex of Ca(1S)–HCl through exciting the Ca atom by a photon. However, the detection of the electronic ground state for CaCl products is particularly difficult [35-37]. Even so, Visticot et al.[38] still successfully probe the complex of Ca–HCl by perceiving the existence of the fluorescence of CaCl in the experiment based on a supersonic beam/laser-ablation. Several calculational investigations are also presented for the Ca+HCl reaction. Verbockhaven et al.[39] constructed the analytical potential energy surface (APES) based on a coupled-cluster as well as the multi-reference configuration-interaction (MRCI) calculations. The APES reliability was confirmed by comparing the quantum-dynamics calculation results based on the obtained APES with the available experimental data. Then, some calculations of quantum reactive-scattering were carried out by Sanz et al.[40] with 0.2–1.0 eV collision energies. They also accessed the quality of the APES of Ca+HCl by comparing their calculational values with the experimental results.

However, the reported investigations on the reaction of Ca+HCl largely involve in the scalar properties, for example, cross-section, rate constant, and product population distributions. Nevertheless, only a few reports about the reaction stereodynamics are presented in the literature. By using the QCT method and the APES of Verbockhaven et al[39], Wang et al.[41-43] studied the rotational momentum alignment of the CaCl product for the Ca+HCl reaction. They have found that the isotopy effect and vibrational state of the HCl reagent can significantly impact on the stereodynamics properties. However, the effect of the different initial rotational states was considered and those of the excited states were omitted. In the present work, to more completely comprehend the stereodynamics properties of the Ca+HCl reaction, we carry through more systematical investigations on the generalized polarization-dependent differential cross-sections (PDDCSs) as well as the rotational momentum orientation and alignment of the HCl molecule.

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

2.1 Rotational polarization of product

The calculational formulas for the polarization of the product’s rotational momentum for the “harpoon-like” model reaction can be found elsewhere[44-48]; in this work, only the basic definition of the vectors are given briefly. Fig. 1 shows the center-of-mass frame (CMF) that we will use in the following discussion. Here ***j′*** represents the product’s rotational angular momentum. ***k*** represents the reagent’s relative velocity vector and ***k′*** is the relative velocity vector of the product. The scattering plane including ***k*** and ***k′*** is located in the*x-z*plane and parallel to the *z*-axis.  is used to symbolizes the angle between ***k*** and ***k′***. The polar and azimuthal angles of the final rotational angular momentum ***j′*** of the product are stood for by  and , respectively*.*

The ***k****-****j′*** correlation can be expressed with the distribution function  which is usually calculated by an expansion of Legendre polynomials. The expanding coefficients in the practical calculations are known as alignment (*k* is even) or orientation (*k* is odd) behavior. The ***k****-****k′****-****j′***correlations are described by the dihedral angle distribution function  which is expanded by the Fourier series. In the present work, the good convergent results can be achieved when the expansive series for, , and reach *k*=7, 18, 24, respectively,

The fully correlated CMF angular distribution is written as

. (1)

In the formula, is PDDCS. A number of photon-initiated experiments for bimolecular reaction demonstrate the measurement is only sensitive to the polarization moments with *k* smaller than 2. Therefore, in this paper, we only calculate , , , and 

**2.2 Quasi-classical trajectory theory**

The stereodynamic properties can be evaluated based on the quasi-classical trajectory (QCT) theory.[41-45，48-51] Three-dimension numerical integration is used to calculate the classical Hamiltonians; the total angular momentum and total energy conservations of every trajectory are used to assure the accuracy. However, QCT has some well-known drawbacks, such as lack of quantum-mechanical effect, omission from non-adiabatic transitions, as well as tunneling, resonance, and zero-point-energy problem. Especially, many researchers have proposed strategies to approximately treat zero-point energy. In the present work, we employ a passive method to treat the zero-point energy, in which all the reactive trajectories with the total vibrational energy of the product below the zero-point energy of the product are discarded. For this reason, the present QCT calculations for the Ca+HCl reaction is acceptable.

For each reaction, we ran 20,000 trajectories totally with the time step of 0.1 fs in the integrations. The collision energy of 0.8 eV is used and the vibrational state remains the ground state for all the considered reactions. Four rotational states as *j*=0, 1, 2, 3 of the HCl molecule are considered. The initial separation distance between the mass center of HCl and the Ca atom is 30.0 Å for every trajectory. The impact parameter *bmax* is tested by a small batch of trajectories. Finally, 2.0, 2.0,1.9, and 1.8 Å are used separately in the four Ca+HCl (*v*=0, *j*=0~3) reactions.

3 **|** **RESULTS AND DISCUSSIONS**

The ***k-j′*** correlations can be described with the  distribution. By using a collision energy of 0.8 eV, we have determined the  distribution of the product for the Ca+HCl reactions with the vibrational and rotational states of *v*=0, *j*=0-3. The results are shown in Fig. 2. The figure demonstrates that the calculated  results symmetrically distribute around =90°, and an obvious peak is observed at 90°. The results mean that the powerfully aligned behavior of the ***j′*** ofCaClis obvious, at the same time, the alignment direction perpendicular to ***k****.* This result shows that the rotational-excited states of the HCl reactant bring about an influence on the stereodynamics properties of the Ca+HCl reaction. One can also find that the initial rotation states of HCl can affect the shape of the  peaks. The peaks become narrower and higher when the rotation excitations are strengthened to *j*=2, which implies that the rotational alignment of CaCl starts to be more obvious. However, the  of the product changes into a wider but lower peak when the rotational state further is excited to *j*=3, implying the rotational alignment of CaCl comes to be weaker. In other words, the rotational alignment effect does not show a monotonic change tendency and the strongest one is identified in the first rotational-excited state. After carefully analyzing, we find the expectation values of is responsible for the interesting results. The calculated expectation values of  for the considered *k* in the present calculations are -0.495977, -0.496644, -0.477073, and -0.45373. By the way, -0.5 of <> means that ***j****′* trends to be polarized perpendicular to ***k***. Obviously, the second expectation value of -0.496644 is the largest and most close to -0.5 one among the four expectations, which confirms the conclusion from the  distributions in Fig. 2.

The ***k*-*k′-j′*** correlation, which is evaluated with the dihedral angle distributions, can be used to further demonstrate the stereodynamics properties. The calculated results of the dihedral angle distributions are illustrated in Fig. 3. The result obviously shows that the dihedral angle distributions of the considered rotational excited states are similar. The common characteristic of  is symmetrically distributed around , implicating all the rotational-exited states bring about the strong angular momentum polarization. If each rotational state is concerned, the peak at  displays obviously larger height than that at . This result means that the  of CaCl inclines to align to the minus direction of the *y*-axis. One can also observe that the peak at  tend to become lower with the increasing of the rotational state *j* of CaCl, indicating that the orientation effect weakens with increasing of *j*. The polarization effects can also understand through the relationship of the angular momentums. The  of CaCl is relative to the ***L*** and ***J*** according to the following equations. [50, 51]

, (2)

, (3)

, (4)

where,  represent unit vectors, while ***L*** represents the orbitalangular momentum of reactant. At the same time, ***j*** stands for the rotational angular momentum of the reactant molecule. is used to stands for the reduced mass of the HCl molecule; ***ER*** in equation (4) represents the repulsive energy. In the processes of the chemical bond breaking as well as forming in the Ca +HCl reaction, one can notice that  is symmetric. However,  occurs in a predominant direction which brings about the orientation of the product molecule of CaCl due to the effect of repulsive energy.

A more visual plots base on the  distribution is presented in Fig. 4 to comprehensively demonstrate the stereodynamics effect in the Ca+HCl reaction. The peaks at  and  have been observed for all  , which correspond to the result for the separate or discussed in the above paragraph. However, the figures based on the distributions give more information, which implicates that the polarization of the CaCl molecule is likely perpendicular to the scattering plane. After carefully examining the figure, we also find that the left-handed rotating in the plane parallel to the *x-z*plane is obviously dominant for the CaCl molecule in the present reaction.

The ***k-k′-j′*** correlations are also relative to the scattering direction of CaCl, which can be evaluated by PDDCSs which are the expected values of ,.ie., (*k*, *q*≤2). However, we first talk about the differential cross-sections (DCS). In fact, DCS depicts the ***k-k′*** correlations and the scattering directions of CaCl without involving in the orientation or alignment of ***j′***. DCS can be evaluated with . Carefully examining the DCS results in Fig .5(a), one can find that the lower excited rotational states ( *j*=0, 1, 2) impact a little on DCS but the *j=* 3 one plays a significant role on DCS. Interestingly, the distinct scattering directions alternate for *j*=0-3. For the Ca+HCl reactions involving in the vibrational ground state and rotational states of 0-2, either forward or backward scattering is strong for the product of CaCl molecule, but the sideway scattering is weak. However, both forward and sideway scatterings are strong for the reaction of Ca+HCl (*v*=0，*j*=3). One can say that the forward scattering could be strengthened along with the increasing of *j*.

Now, let us throw our light on the parts of PDDCSs based on the second Legendre moments. The calculated result is shown in Fig. 5(b), demonstrating that show the opposite trend in the ranges of the scattering angle smaller or larger than 90° of , which implies that ***j′*** likely aligns perpendicular to ***k***. Moreover, at =180°, ***j′*** inclines to be polarized toward the direction perpendicular to ***k***. For majority regions of the scattering angle, Fig.5(b) shows that the values are minus, implicating that the ***j****′* of CaCl inclines to align along with the *y*-axis. The strongest polarizations of ***j****′* are at approximately 38° and 142°. The result for the of PDDCS relative to in Fig. 5(c) demonstrates all the initial rotational states of *j*=0-3 of the reactant can induce the polarization for the product, and that of *j*=3 is more obvious than those of the other reactions. In sum, the distributions of ***j****′* are significantly affected by the initial rotation states, which implies that the stereodynamics phenomena in the Ca + HCl(*v*=0, *j*=0- 3) reactions are obvious.

1. **CONCLUSIONS**

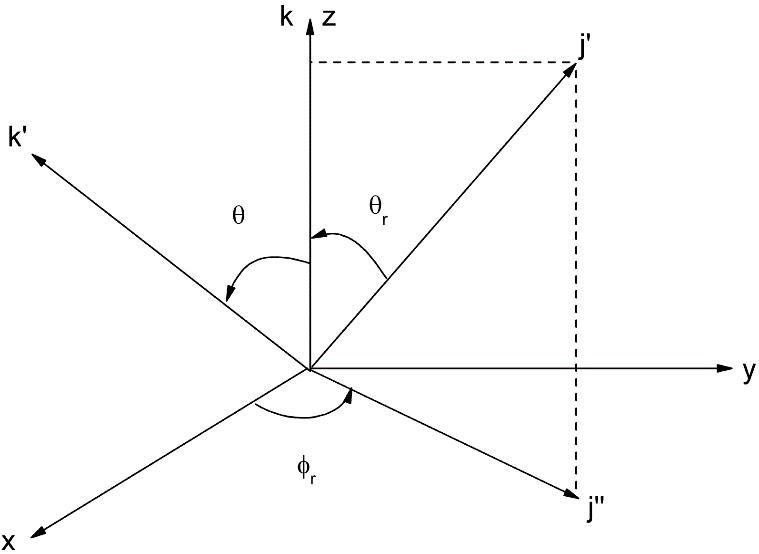
The influence of the rotational-excited states of the reactant molecule HCl on the stereodynamics properties of the harpoon-like molecular reaction of Ca + HCl(*v*=0, *j*=0-3) is examined by QCT. The rotational quantum numbers impose a considerable effect on vector correlations, including alignment, orientation, and PDDCSs. The first rotational-excited state plays the strongest role on the product’s alignment, and the orientation comes to be weak with increasing *j*. Moreover, the ***j***′ of the product CaCl molecule shows obvious alignment, at the same time, oriented toward the negative direction of the *y*-axis. The CaCl molecule shows different scattering characteristics including strong forward or backward scattering as well as weak sideway-scattering for the different initial rotational states of the reactant molecule. Moreover, the strong forward scattering is only recognized for the higher-rotational-excited state of the reactant. Furthermore, PDDCSs are influenced by the initial rotational states of the reactant, which confirmed the vector correlation performance in the title reaction. These findings could provide helpful information to understand the microscopic mechanism of the harpoon-like molecular reaction of Ca+HCl→CaCl+H.

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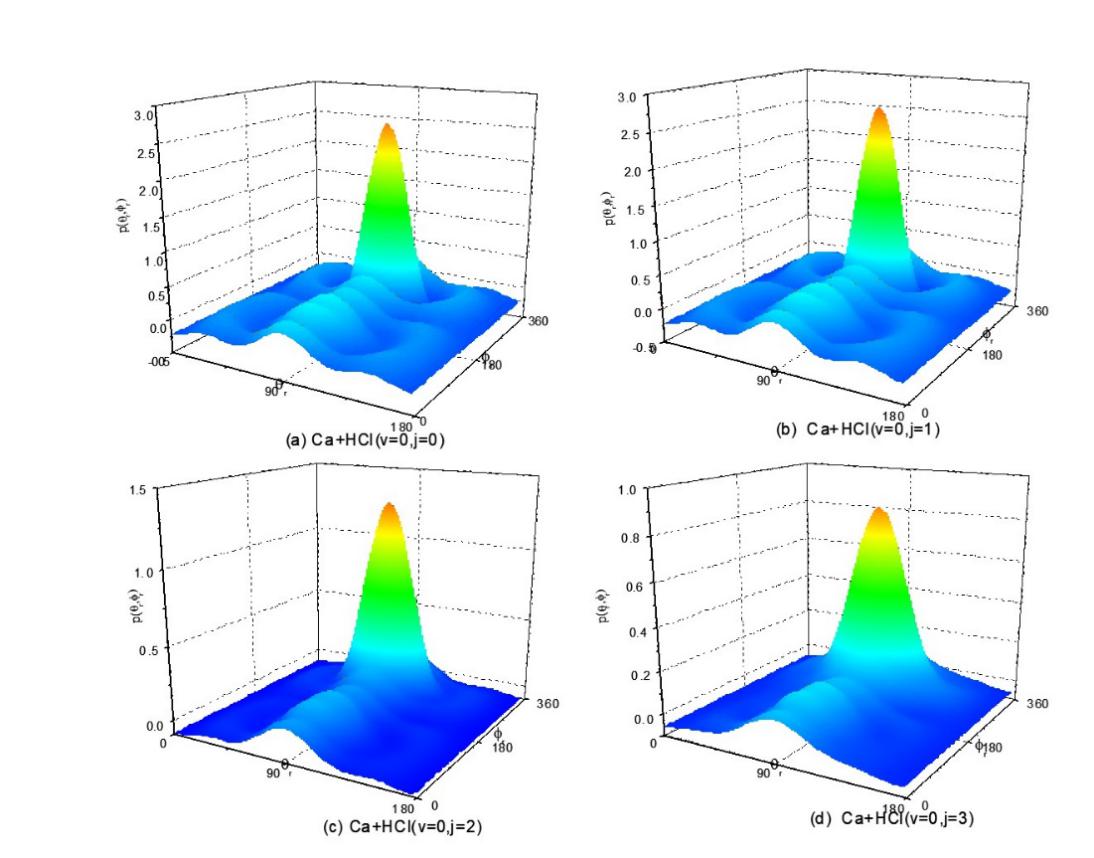
**FIGURE 1.** The center-of-mass coordinate system for the description of ***k, k*′** and ***j*′** correlations.



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



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



**FIGURE 4.** Polar distributions of  averaged over all scattering angles. (a), (c), (b) and (d) are for the reactions of Ca+HCl with *v*=0 and *j*=0, 1, 2, 3, respectively.





**FIGURE 5.** PDDCSs. (a) for ; (b)–(d) for, respectively.

1. \*Corresponding author. *E-mail address:* ycl@ldu.edu.cn. (C.L. Yang). [↑](#footnote-ref-1)