Eur. Phys. J. D **24**, 169–172 (2003)
DOI: 10.1140/epjd/e2003-00142-5

**THE EUROPEAN
PHYSICAL JOURNAL D**

A theoretical study on electron transfer in low-energy collisions of a collinear meta-stable Na_3^+ with a Na

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Received 10 September 2002

Abstract. Electron transfer in the collisions of a Na_3^+ with a Na is theoretically studied. It is assumed that the target Na_3^+ is collinear ($D_{\infty h}$) and that its electronic state is meta-stable triplet ($a^3\Sigma_u^+$) state. Adiabatic potential energy surfaces and non-adiabatic couplings of the Na_4^+ system are calculated by using a semi-empirical diatomics-in-molecules (DIM) method. The positions of (avoided)-crossings of potential surfaces are investigated and the non-adiabatic couplings between two different electronic states are calculated. An avoided crossing is found in the region where the separation between the target and projectile is relatively large (10–15 bohr). A dynamical calculation demonstrates that this crossing causes charge transfer between the target and projectile. Another intersection at a smaller separation changes the target's spin state (from triplet state to singlet state or *vice versa*). The cross-sections for charge and spin transfer reaction are estimated at the collision energy of 6.8 keV. It is found that the charge transfer cross-section is extremely enhanced when the target cluster ion is in its meta-stable triplet state comared to the case where the cluster is the ground singlet state.

PACS. 36.40.-c Atomic and molecular clusters – 36.40.Cg Electronic and magnetic properties of clusters – 34.70.+e Charge transfer

1 Introduction

An enormous amount of works has been devoted to the study of electronic transfers both in atom-ion collisions [1] and surface-ion collisions [2,3]. To bridge the gap between two well established fields, there have been some recent experiments to study the charge transfer between clusters and atoms/ions. For example, the cross-section of the charge transfer in the collision between alkali-metal cluster ions and alkali-metal atoms have been systematically measured by Bréchignac and coworkers [4–6]. Various types of theoretical approaches have been made on this problem. The first principle calculation such as non-adiabatic quantum molecular dynamics (NAQMD) have been done [7–9]. Within the framework of the jellium model [10–12], Zarour *et al.* [12] calculated the CT cross-section in the collisions of alkali-metal cluster ions and atoms in good agreement with the experiment [5]. Phenomenological models such as the Hubbard model, including our previous work [13], give some physical insights on what is going during the collision.

In this article, we study the charge transfer between an atom and a cluster-ion through the picture conventionally used in ion-atom, molecule collisions. We describe the charge transfer in terms of an adiabatic picture. This approach would be valid in low energy collisions in which the speed of the projectile is small enough compared those of electrons. For this purpose, the evaluation of accurate potential surfaces including those for excited states and the calculation of non-adiabatic couplings are necessary. Both of them are difficult to calculate for most of the cases. We simplify these procedures by using an approximate electronic theory as has been used by Babikov *et al.* [14] in the study of collision induced fragmentation of sodium clusters. Although our calculation is not fully *ab initio*, the result would be accurate enough for our purpose.

As an illustrative example, the collision of a Na_3^+ with a Na is chosen. For this system, Roller-Lutz *et al.* measured the charge transfer cross-section and they also made theoretical calculation by using the NAQMD [7]. In their case, it is assumed that the shape of Na_3^+ is equilateral triangle (D_{3h} in the symmetry group notation) and its electronic state is the ground singlet state ($X^1A_1^{'}$). Contrary to their treatment, here we shed light on the case where the target Na_3^+ is collinear with the inversion symmetry ($D_{\infty h}$) and its electronic state is meta-stable triplet state ($a^3\Sigma_u^+$). As for Na_3^+, it is well known that the D_{3h} configuration is geometrically most stable for X state. On the other hand, as for triplet a state, the $D_{\infty h}$ configuration is found to be the most stable [15]. Cluster ions are usually produced by electron or photon impacts to neutral

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clusters. If the impact energy is enough high, it is expected that not only ground state but also excited cluster ions will be produced. Since meta-stable clusters survive for a relatively long time under collision free conditions. Thus it is important to study on the reactivity of excited states of clusters. As we shall see later, the reactivity of meta-stable state is completely different from that of the ground state.

In this article, we discuss the properties of the electronic states and non-adiabatic interaction responsible for electronic transfer. Then we will demonstrate some results of typical dynamical calculations. The atomic unit is used throughout this article unless otherwise stated.

2 Method

Here we mainly consider the following charge transfer (CT) reactions

$$\mathrm{Na}_3^+(a^3\Sigma_u^+) + \mathrm{Na}(^2\mathrm{S}) \rightarrow \mathrm{Na}_3(X^2\Sigma_u^+) + \mathrm{Na}^+(^1\mathrm{S}). \qquad (1)$$

The following “spin transfer”(ST) reaction takes place simultaneously,

$$\mathrm{Na}_3^+(a^3\Sigma_u^+) + \mathrm{Na}(^2\mathrm{S}) \rightarrow \mathrm{Na}_3^+(X^1\Sigma_g^+) + \mathrm{Na}(^2\mathrm{S}). \qquad (2)$$

Note that the change in the spin state of the target is due to an electron exchange. The heat of reaction ΔE for these reactions depends on the nuclear configuration. In our case, we estimated as -0.022 and 0.016 Hartree for (1) and (2), respectively by using the method mentioned below. For comparison, we will also study both the CT and ST reactions when the Na_3^+ is the ground state.

First, let us make adiabatic potential surfaces of the system to describe these reactions. Here, a semi-empirical Diatomics-in-Molecules (DIM) method is used to calculate the potential energy surfaces. The DIM was first proposed by Elison [16], and developed by Tully [17], Kunz [18] and others. With this method, we can calculate both potential energies and non-adiabatic couplings with far less efforts compared to the other methods. Since the DIM method has been stated in detail in many articles (see [18] for example), we mention only the outline of the method. In the DIM, the total electronic Hamiltonian H_{el} is composed as a sum of those of the diatomic fragments H_{PQ} and atomic fragments H_P, namely,

$$H_{el}(\mathbf{q};\mathbf{R}) = \Sigma H_{PQ} - (N-2)\Sigma H_P, \qquad (3)$$

where N denotes the number of atoms in the systems, $\mathbf{q}$ and $\mathbf{R}$ indicate the positions of electrons and nuclei, respectively; the summation must be carried for all the atoms and diatomic pairs. An eigenenergy $\epsilon_i(\mathbf{R})$, as a function of a nuclear position $\mathbf{R}$ (here we label the state by a suffix i) is obtained by solving the equation

$$(H_{el}(\mathbf{q};\mathbf{R}) - \epsilon_i(\mathbf{R}))\phi_i(\mathbf{q};\mathbf{R}) = 0. \qquad (4)$$

The adiabatic electronic wave function ϕ_i is expressed as a linear combination of basis functions shown in Table 1.

Table 1. The DIM basis set used in the present calculation. In the table, a, b, c and d denote the 3s orbitals locate the atom A, B, C and D, respectively.

base	wave function
Ψ_{a1}	$\frac{1}{\sqrt{2}}(\lvert bc\bar{d}\rvert - \lvert b\bar{c}d\rvert)$
Ψ_{a2}	$\frac{1}{\sqrt{6}}(2\lvert \bar{b}cd\rvert - \lvert bc\bar{d}\rvert - \lvert b\bar{c}d\rvert)$
Ψ_{b1}	$\frac{1}{\sqrt{2}}(\lvert cd\bar{a}\rvert - \lvert c\bar{d}a\rvert)$
Ψ_{b2}	$\frac{1}{\sqrt{6}}(2\lvert \bar{c}da\rvert - \lvert cd\bar{a}\rvert - \lvert c\bar{d}a\rvert)$
Ψ_{c1}	$\frac{1}{\sqrt{2}}(\lvert da\bar{b}\rvert - \lvert d\bar{a}b\rvert)$
Ψ_{c2}	$\frac{1}{\sqrt{6}}(2\lvert \bar{d}ab\rvert - \lvert da\bar{b}\rvert - \lvert d\bar{a}b\rvert)$
Ψ_{d1}	$\frac{1}{\sqrt{2}}(\lvert ab\bar{c}\rvert - \lvert a\bar{b}c\rvert)$
Ψ_{d2}	$\frac{1}{\sqrt{6}}(2\lvert \bar{a}bc\rvert - \lvert ab\bar{c}\rvert - \lvert a\bar{b}c\rvert)$

In the system now we are studying, the total electronic spin of the system is limited to be 1/2.

We check the reliability of the method including the choice of the basis set by calculating the equilibrium distance of the collinear a state Na_3^+ and the heat of the reaction of (1). We obtain the equilibrium internuclear distance of $r_e = 7.22$ (bohr). This value is slightly shorter than the value 7.41 (bohr) obtained in accurate calculation by Bonačic-Koutecký *et al.* [15]. At our equilibrium configuration, we have the heat of reaction -0.022 (-0.025) Hartree in the DIM (*ab initio*) calculation. We see that the present DIM calculation reproduces the results of *ab initio* calculations with a considerable accuracy.

Non-adiabatic coupling such as $\mathbf{f}_{ij} = \langle\phi_i|\nabla_{\mathbf{R}}|\phi_j\rangle$ is easily calculated by using the way shown by Tully [17]. All what we need is the potential curves of diatomic molecules. As for Na_2 and Na_2^+, they are calculated by Bardsley *et al.* [19], Mannier*et al.* [20] and so on and their analytical expressions have been given by Kunz [21].

Once the potential energies and non-adiabatic couplings are given, and if we assume that the nuclear motion is classical *i.e.* $\mathbf{R} = \mathbf{R}(t)$, we solve the time-dependent Shrödinger equation, $\mathrm{i}\mathrm{d}\Phi/\mathrm{d}t = H_{el}\Phi$, by expanding the total wave function Φ in terms of adiabatic electronic wave functions ϕ_i as

$$\Phi = \sum_j c_j\phi_j(\mathbf{q};\mathbf{R}(t)) \exp\left[\mathrm{i}\int_{-\infty}^{t} \epsilon_j(\mathbf{R}(t'))\mathrm{d}t'\right], \qquad (5)$$

where c_j denotes the amplitude for jth electronic states. We have the following coupled equation,

$$\frac{\mathrm{d}c_j}{\mathrm{d}t} = -\sum_i \frac{\mathrm{d}\mathbf{R}}{\mathrm{d}t}\mathbf{f}_{ij} \exp\left[\mathrm{i}\int_{-\infty}^{t} (\epsilon_j(\mathbf{R}(t')) - \epsilon_i(\mathbf{R}(t')))\mathrm{d}t'\right] c_i. \qquad (6)$$

We can evaluate the transition probabilities by solving this equation with an appropriate boundary condition.

3 Results of computations

We take a coordinate system as shown in Figure 1: the origin at the center of the target cluster, the x-axis along

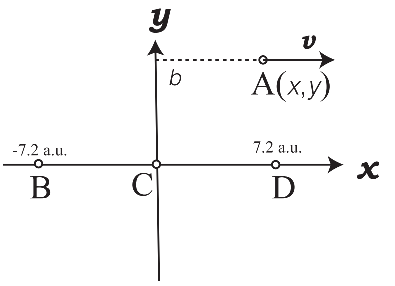

Fig. 1. Collision geometry of the system.

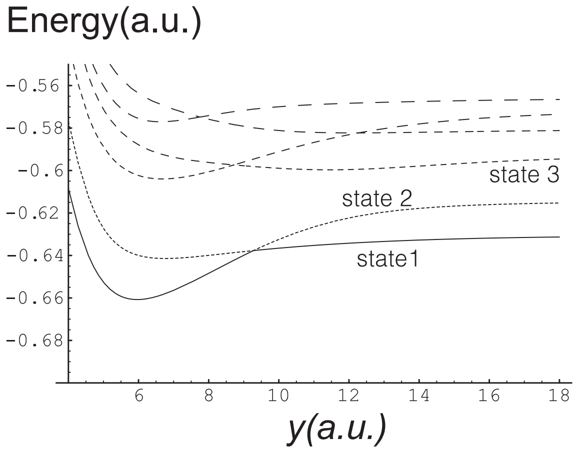

Fig. 2. Potential curves of the T-shaped Na_4^+ system as functions of y.

the molecular axis, and y-axis perpendicular to the molecular axis; the bond length $r_{BC} = r_{CD}$ is taken to be 7.2(2) a.u. The position of the projectile is shown by (x, y). In Figure 2, we present adiabatic potential curves of a T-shaped Na_4^+ system as a function of y. At the infinite separation, $(y \to \infty)$ the energetically-lowest, the next to the lowest and the thirdly lowest state correspond to $\mathrm{Na}_3^+(X^1\Sigma_g^+)+\mathrm{Na}(^2\mathrm{S})$, $\mathrm{Na}_3^+(a^3\Sigma_u^+)+\mathrm{Na}(^2\mathrm{S})$ and $\mathrm{Na}_3(X^2\Sigma_u^+) + \mathrm{Na}^+(^1\mathrm{S})$, respectively. These three states are the most important in the reactions. Hereafter, we refer them to state 1, state 2 and state 3, respectively. In this notation, the CT reaction (1) corresponds to the transition from state 2 to state 3 and the ST reaction (2) transition from state 2 to state 1. From the figure, it is clear that states 1 and 2 intersect each other $y \simeq 9$. States 2 and 3 make an avoided crossing around $y = 12{-}15$. Although it cannot be well recognized by Figure 2, the situation will be clearer through the strength of non-adiabatic couplings between the two states (Fig. 3).

In Figure 3, we show the strength of the non-adiabatic couplings between two different electronic states $f_{ij} = |\mathbf{f}_{ij}|$ for $(i, j) = (1, 2)$, $(1, 3)$ and $(2, 3)$ along the line $x = 0$. We see that the non-adiabatic coupling between states 1 and 2 is extremely large around the intersection $(y \simeq 9)$. The coupling between states 2 and 3 has a peak in the region of $y = 10{-}15$ a.u. This is an evidence that these two electronic states are making an avoided crossing in this region. The coupling between states 1 and 3 is always smaller compared to the previous two couplings.

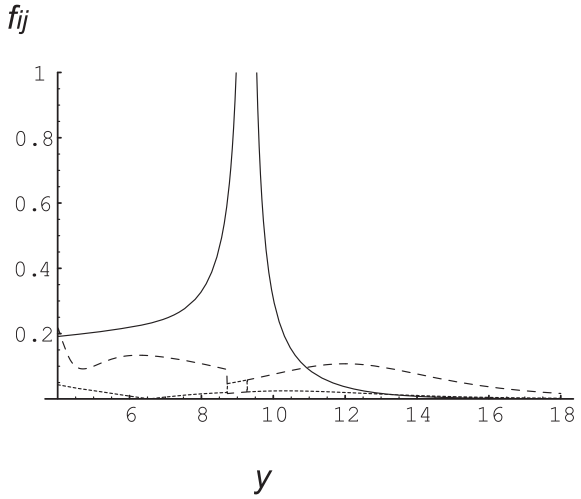

Fig. 3. The non-adiabatic couplings $f_{ij} = |\langle\phi_i|\nabla_{\mathbf{R}}|\phi_j\rangle|$ along the path $x = 0$ as functions of y. Solid, dotted and dashed lines represent, respectively, for $(i, j) = (1, 2)$, $(1, 3)$ and $(2, 3)$.

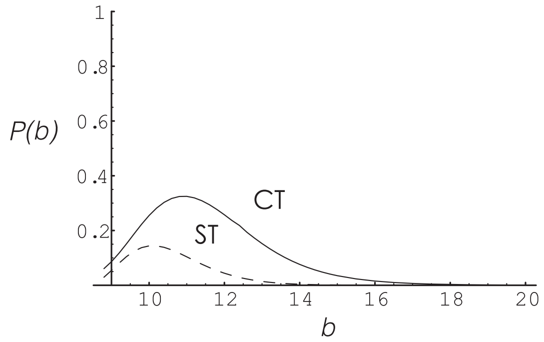

Fig. 4. The transition probability $P(b)$ *vs.* the impact parameter b at the collision energy of 6.8 keV for the case where Na_3^+ is meta-stable a state. Solid and dashed lines represent that for the charge transfer and spin transfer, respectively.

Finally, we demonstrate a result of the dynamical calculation. As shown in Figure 1, here we assume that the motion of the projectile is parallel to the molecular axis *i.e.* $y = b$ (constant) with a constant speed $v = 0.126$ (a.u.), which corresponds to collision energy of 6.8 keV in the center of mass system. We also assume that every atom in the target do not move during the collision. Since we have made these simplifications, we will not able to treat the processes concerning nuclear motions in the cluster, such as fragmentation of clusters. Thus here we demonstrate the results of only *distant collisions* for which the impact parameter b exceeds 9 a.u. In Figure 4, we plot the probabilities of CT and ST as functions of the impact parameter b for the case where the Na_3^+ is metastable. We see that each transition probability has a peak around each crossing region. From this calculation, we can estimate the CT (ST) cross-section as 87(24) bohr^2. This estimation is a little bit crude since the atomic configuration is fixed and only the contributions of distant collisions are taken into account.

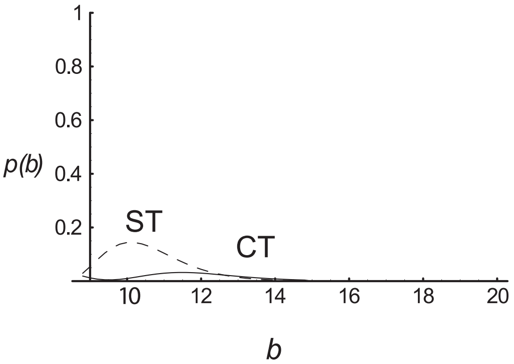

Fig. 5. The same figure as Figure 4 for the case where Na_3^+ is the ground X state.

To make a comparison, we also show the results of the case where the Na_3^+ is the electronic ground state ($X^1\Sigma_g^+$), with keeping the same geometrical symmetry ($D_{\infty h}$). Figure 5 shows the CT and ST probabilities as functions of impact parameter b for the case where Na_3^+ is X state at the same collision energy as the previous one. We see that the ST probability as a function of b shows nearly the same tendency as the case of a state while CT probability is much smaller for every region of b. The CT(ST) cross-section for the ground state is estimated as 8(24) bohr^2. Compared to the case of a state, ST cross-section is nearly the same and CT cross-section is much smaller for X state.

According to the NAQMD calculation made by Roller-Lutz *et al.* [7] the CT cross-section for the ground state Na_3^+ with D_{3h} symmetry is about 25 bohr^2 at the collision energy of 5 keV. Since our collision energy is slightly higher than theirs, we cannot make a direct comparison with them. It is probable, however, that the CT cross-section for meta-stable a state with $D_{\infty h}$ symmetry would be larger that for the ground X state with D_{3h} symmetry. They have also shown that the CT cross-section is much enhanced when the Na atom is excited. In our case, not the atom but the cluster is excited. Our result show a common tendency with them that the electronic excited state is more favorable for charge transfer than the ground state.

4 Conclusions

We have studied the electron transfer reactions in the collisions of collinear a state of Na_3^+ with Na. Using the DIM method, the characters of adiabatic potential surface and non-adiabatic couplings are revealed. Two crossings are found to be important for the transitions. One causes the charge transfer from target to projectile and another spin transfer. It is also found that the CT cross-section is much large for the meta-stable triplet state than for the ground singlet state.

We are grateful to Prof. Sidis's group for valuable comments during this work.

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