Dipped Adcluster Model Study of Surface Reactions

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Abstrat. Dipped adcluster model (DAM) for surface reactions involving electron transfer between admolecule and surface and the SAC/SAC-CI method for studying many different electronic states are explained and applied to harpooning, surface chemiluminescence, and electron emission in the halogen chemisorption on alkali-metal surfaces.

1. Introduction

For theoretically studying reactions on a metal surface, the first question is "how do we describe surface-molecule interaction in a tractable way ?". When admolecule-surface electron transfer is important, the cluster model (CM) may be inadequate. We have proposed dipped adcluster model (DAM) [1] in which the adcluster, which is a combined system of an admolecule and a cluster, is dipped onto the electron bath of the solid metal and an equilibrium is established for an exchange of electrons between the adcluster and the bulk metal. Electrostatic image force, characteristic to a metal surface, is also included [2]. Furthermore, for quantitative descriptions of molecule-surface interactions and reactions, electron correlations, electron transfers, and participations of lower exited states are very important. The SAC (symmetry adapted cluster)/SAC-CI method [3-5] is very suitable for such studies because it describes ground, excited, ionized, and electron attached states efficiently in a similar accuracy [3].

The DAM has been applied to oxygen chemisorptions on palladium [1,2] and silver [6] and halogen chemisorptions on alkali metal surfaces [7]. In the latter, the harpooning, surface chemiluminescence and surface electron emission were nicely explained in agreement with experiment. We further applied the DAM to silver-catalyzed partial oxydation of ethylene [8]. We give here a brief review of such studies.

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2. Dipped Adculster Model (DAM)

For surface-molecule interacting systems in which electron transfer between surface and admolecule is important, the CM is insufficient, because the cluster itself must supply or accomodate electrons to or from the admolecule by strongly affecting the bonds of the cluster itself, if the cluster is small. In actual metal surfaces, a sufficient number of free electrons exist, so that the transfer of electron to or from the admolecule does not significantly affect the local bonding of the metal atoms of the cluster directly interacting with the admolecule.

There are many cases in which electron transfer seems to be very important; oxygen and halogen chemisorptions on a metal surface, the roles of alkali metals and halogens as promoters of catalytic reactions, and the activity of the electropositive metals for dissociative adsorptions of CO, N_2 etc. The dipped adcluster model (DAM) [5,6] has been proposed for dealing with such systems.

Fig. 1 illustrates the concept of DAM. We define "adcluster" as a combined system of admolecule and cluster. We dip it into the electron "bath" of the solid metal and let an equilibrium be established for the electron and/or spin transfer between them. The equilibrim would be established when the chemical potential of the adcluster becomes equal with the chemical potential of the surface, or more precisely when the adcluster reaches at the minimum of $E(n)$ in the range of

$$-\frac{\partial E(n)}{\partial n} \geq \mu \qquad (1)$$

where $E(n)$ is the energy of the adcluster, n is the number of electrons transferred from the bulk metal to the adcluster, and μ is the chemical potential of the electrons of the metal surface. Since the adcluster is a partial system, the number of the transferred electrons, n, is not necessarily an integer. In this model, the external effects such as those of promoters, cocatalysts, supports, temperature, electric potential, etc., are included through a variation in the chemical potential μ.

A typical behavior of the $E(n)$ curve is illustrated in Fig. 2. The $E(n)$ curve is a lower convex in case (a), but an upper convex in case (b). In case (a), electron flows

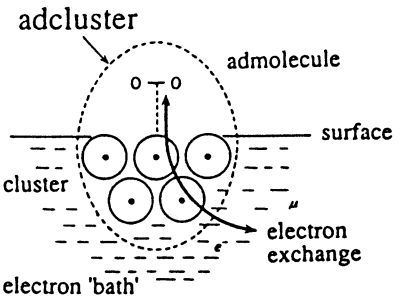

Fig. 1 Concept of the dipped adcluster model (DAM).

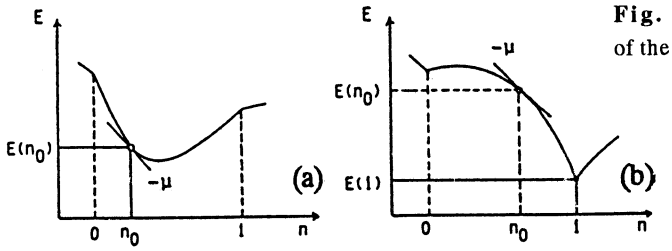

Fig. 2 Two examples of the *E(n)* curve.

into the adcluster up to n_0, where the gradient of the *E(n)* curve becomes equal to -μ, as eq(1) implies, since the potential of the adcluster is lower than that of the electron of the metal. The energy of the adcluster is $E(n_0)$. In case (b), there is a barrier to electron flow: electron flow does not occur until n_0 electrons "sink" into the adcluster through, say, tunneling or activation, but afterwards, the electron looks down a deep valley and flows into it up to *i*, as eq(1) indicates, *i* being an integer. At $n=i$, the system is most stable, and when n exceeds *i*, the potential suddenly becomes very high (even positive), so that electron flow ceases at $n=i$. The energy of the system is $E(i)$. It is interesting to note that in case (b), transfer of an integral number of electrons naturally results, so that the case (b) is, in some senses, quantum. When the gradient of the *E(n)* curve does not become equal with -μ in some range of *n*, the electron flow does not occur. For more details, see ref. [1].

The energy of the adcluster *E(n)* may be calculated by the molecular orbital (MO) method [1] or by the method including electron correlations [3-5]. The density-functional method [9] is also applicable to this purpose. In the MO method described in ref 1, we assumed that the adcluster exchanges electrons and spins with the solid through the active orbitals of the adcluster: e.g. highest occupied (HO) MO and the lowest unoccupied (LU) MO.

On a metal surface, the electrostatic force, called image force, is sometimes very important. This is especially so when the system involves a large amount of electron transfer. In the DAM, the image force effect is rather easily included [2] based on the theory of electricity.

3. SAC/SAC-CI Method

Electron correlations are sometmes very important for the surface phenomena. In particular, when the surface is a transition metal, the Hartree-Fock model is insufficient for describing the bonding between admolecule and surface. Furthermore, since the catalytically active states are not necessarilly the ground states of the system. Excited states are sometimes responsible for the reaction [6,10]. Therefore, we need a theory which can describe both ground and excited states in a same accuracy. The SAC/SAC-CI theory is such a theory.

The SAC theory [4] provides a method for calculating a ground state and the SAC-CI method [5] is the method for calculating correlated wave functions for excited, ionized, and electron attached states. The SAC/SAC-CI wave functions satisfy the correct relations among these states and are based on the approximate transferability of electron correlations among these states. The SAC/SAC-CI method is more rapidly convergent than ordinary CI expansion and furthermore it gives directly comparable results for the energies and the wave functions of many different states, different in energy and in the number of electrons. The theoretical simplicity, reliability, and usefulness have been shown in many publications in molecular spectroscopy [11] and excited state chemistry [12,13]. We believe that the method is simple and accurate enough to be useful. For more details, we refer to a recent review article [3]. The SAC/SAC-CI code [14] is available from the author on request.

4. Halogen Chemisorption on Alkali Metal Surface

Halogen chemisorption on an alkali metal surface involves interesting electron transfer processes from the surface to the halogen molecule, X_2. They are 'harpooning', surface chemiluminescence, and surface electron emission. When a halogen molecule approaches to some distance from the surface, an electron jumps into the molecule: this large distance electron transfer is called 'harpooning'. When the molecule receives an electron, it becomes an anion so that the molecule is elongated and at the same time, it is attracted to the surface. When it collides with the surface, the surface chemiluminescence and electron emission occur. They are the electron transfer processes from the surface to the molecule accompanied with the emissions of a photon and an electron, respectively. Up to three electrons are thus transferred from the surface to the molecule. We investigate these electron transfer processes by the DAM and the SAC/SAC-CI method [7].

4.1 Harpooning

Harpooning is a long-distance jump of an electron from a metal surface to a molecule. It is explained as an electron tunnelling from the alkali metal surface to the halogen molecule. However, in the conventional model, this process should be strongly vibronic, since the electron affinity of X_2 is very much dependent on the X-X distance: a large electron affinity of X_2 is obtained only after an elongation of the distance.

We assume that Cl_2 molecule approaches the surface in the end-on form, since the σ^* MO of Cl_2 is the electron-accepting orbital. We think that the electron transfer occurs as a Franck-Condon process, so that the Cl-Cl distance is fixed to 2.0025 Å, theoretically optimized distance: the experimental equilibrium distance is 1.987 Å. We do not take into account molecular vibration effect. The alkali metal surface is

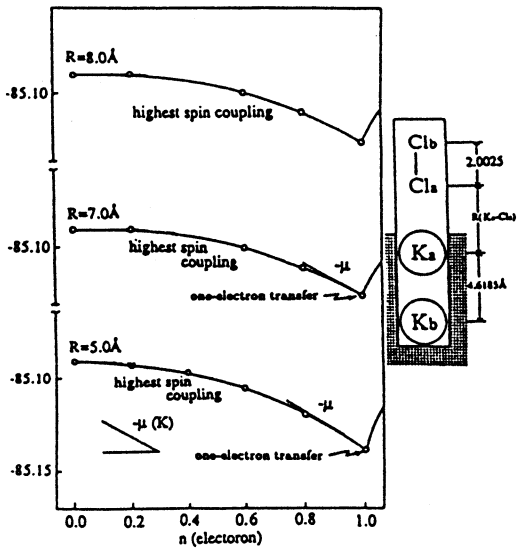

Fig. 3 *E(n)* curves calculated by the DAM for the Cl_2- potassium surface system at the Ka-Cla distances of 8, 7, and 5 Å.

represented by the two metal atoms dipped onto the electron bath of the alkali metal surface as illustrated in Fig. 3. We consider here only potassium surface.

We first apply molecular orbital model for the DAM [1]. The adcluster K_2 interacting with Cl_2 is dipped onto the electron bath of the potassium metal whose chemical potential μ is 2.30 eV. Fig. 3 shows the E(n) curves, calculated at different separations of Cl_2 from the surface. The curve is calculated by the highest spin coupling model [1] and the active orbital is chosen to be the σ^* MO of Cl_2. The E(n) curve is an upper convex and its tangent can become larger (in absolute value) than $-\mu$ when the Cl_a-K_a distance is smaller than 7 Å. Since the E(n) curve is an upper convex, one electron (an integral number, one) is transferred from the surface to Cl_2. This one electron transfer is just the harpooning of an electron from the surface to Cl_2: this is the DAM picture of the harpooning. We note that we could explain the harpooning as a Franck-Condon process without resorting to the vibronic coupling. We also note that we have used the picture of 'tunneling' from E(0) to E(n) in the *n-E* space not in the *R-E* space. Similar results were also obtained for the sodium-Cl_2 and rubidium-Cl_2 systems, giving different harpooning distances [7].

4.2 Elongation and Chemisorption of Cl_2^-

The harpooning occurs as a Franck-Condon process in the DAM, and afterwards, the Cl-Cl distance is elongated to be 2.64 Å with much stabilization of about 48 kcal/mol [7]. The binding energy of Cl_2^- on the surface is calculated to be only 7 kcal/mol: very weak even in comparison with the experimental binding energy, 29

kcal/mol of a free Cl_2^-. Since the energy gain by the elongation is much larger than the binding energy, we expect that a neutral Cl atom is ejected out from the surface after the harpooning. Nevertheless, some Cl_2^- molecule would further adsorbed on the surface, with the excess energy being dissipated somewhere, say, to the alkali metal surface.

4.3 Surface Chemiluminescence Process

Next is the surface chemiluminescence process: the second electron is transferred from the metal surface to the halogen molecule with an emission of a photon. We here assume the reaction pathway of the adcluster K_2-Cl_2^- as shown in Fig. 4. The reaction is assumed to proceed from the end-on geometry on K_a, #1 and #2 positions, to the dissociated chemisorption structures, #8 and #9.

An interesting question here invoked is "from where the second electron originates?". Does it originate from the bulk metal or from the local K_2 site directly interacting with Cl_2? In order to answer this question, we calculated by the SAC/SAC-CI method the total energies of the adclusters with the formal charges of K_2-Cl_2^{2-} and K_2^{2+}-Cl_2^{2-}, the former being the product of the electron transfer from the bulk metal and the latter from the local K_2 site. As a result, we find that the latter is lower than the former. We therefore conclude that the second electron originates from the local K_2 site directly interacting with Cl_2^-.

We calculate the potential energy of the K_2-Cl_2^{2-} adcluster (initial state) and the K_2^+-Cl_2^{2-} adcluster (final state) by the SAC-CI method. Fig. 5 shows the result. The

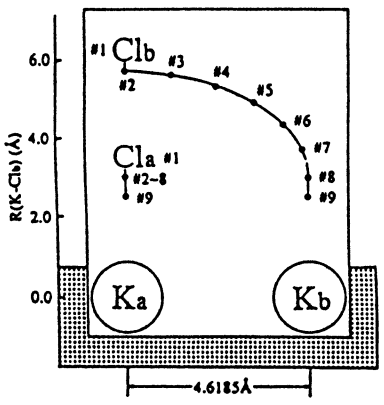

Fig. 4 Assumed reaction pathway for the surface chemiluminescence and electron emission processes.

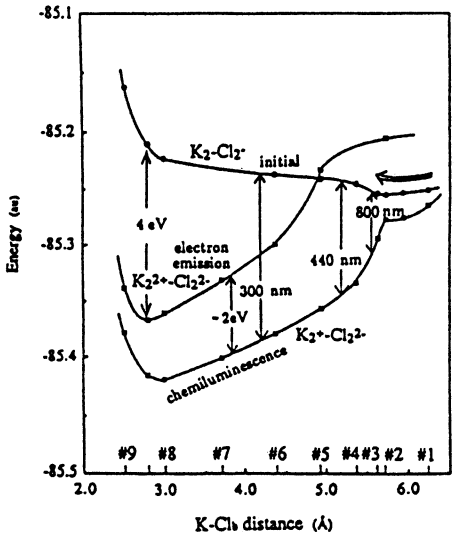

Fig. 5 Potential curves of the Cl_2-potassium surface system for the surface chemiluminescence and electron emission processes calculated by the SAC/SAC-CI method.

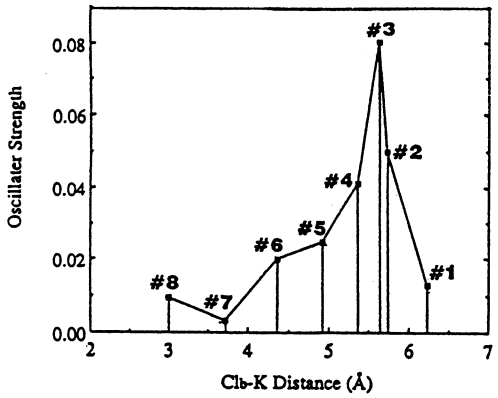

Fig. 6 Oscillator strength for the chemiluminescence along the reaction coordinate.

final state is denoted by 'chemiluminescence'. The figure also includes the final state of the electron emission discussed later. The system proceeds from the right to the left on the initial state curve, as shown by a big arrow, and makes a transition to the chemiluminescence final state with emitting a photon. The energy of the emitted photon is given by the energy difference of the initial and final states plus some kinetic energy of the accelerated Cl_2^- in the initial state. The wave numbers shown in the figure correspond to the former one. Before #5 position, only the chemiluminescence transition occurs, but after there, two channels of transitions exist, namely, the chemiluminescence channel and the electron emission channel. Experimentally, the spectrum spreads from about 800 nm to 300 nm with the peak maximum at about 440 nm [7]. The intensity rapidly decreases from about 400 nm to 300 nm. This rapid decrease is understood to be due to the transition to the electron emission channel: the crossing at about #5 geometry facilitates this transition. Fig. 6 shows the calculated probability of the transition: it is maximum at #3 geometry and decreases in the geometries in either side. Thus, we understand that the transition occurs in the course of the dissociative chemisorption.

4.4 Surface Electron Emission Process

Finally we study the surface electron emission process. This is the two-electron process in which one electron is transferred from the surface to the halogen molecule anion X_2^-, and at the same time, another electron is emitted out of the surface. We assume that these two electrons belong to the local K_2 site directly interacting with Cl_2^-, since they are so strongly correlated in this process. It is difficult to expect such a strong correlation if one or two of these electrons belong to the bulk metal. We use again the reaction path shown in Fig. 4.

Fig. 5 includes the potential curve for the final state of the surface electron emission calculated by the SAC-CI method. The initial state is common to both

processes. The electron emission process occurs later to the chemiluminescence process, since the process proceeds from right to left on the initial-state curve. The emission occurs in the left of the geometry #5, where the initial and final state curves of the electron emission cross to each other. The excess (kinetic) energy of the emitted electron is about 4 eV at the turning point of the initial state curve, #8-#9, which is also the equilibrium geometry of the final state, namely KCl. We therefore expect a large transition probability at #8-#9 geometries from these features of the potential curves: the Franck-Condon factor should be large there. A large transition probability is also expected at the crossing point at about #5 geometry and may be calculated by the Landau-Zener model. Experimentally, the exoelectron energy distributions are measured for Cl_2 on yttrium and on Rb-dosed yttrium, and a maximum peak is seen at about 4 eV in accordance with the above expectation [7].

In Fig. 5, the difference between the final-state potential curves of the electron emission and the chemiluminescence is roughly about 2 eV at any geometry of the reaction pathway. This is because the difference corresponds to the work function of the potassium surface: the experimental value is 2.3 eV.

5. Conclusion

We have investigated various types of surface-molecule interactions by the methodology of our laboratory: the dipped adcluster model and the SAC/SAC-CI method. It is shown that this methodology is powerful for investigating surface-molecule interactions and reactions occurring on metal surfaces in thermal and photochemical situations. Our methodology is also useful for studying surface photochemistry [13].

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