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Dipped adcluster model and SAC-CI method applied to harpooning, chemiluminescence and electron emission in halogen chemisorption on alkali metal surface

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Abstract

The methodology of our laboratory, the dipped adcluster model (DAM) and the symmetry adapted cluster configuration interaction (SAC-CI) method, are briefly reviewed and successfully applied to the electron transfer processes, harpooning, surface chemiluminescence, and surface electron emission, in the course of the chemisorption of halogen molecule on an alkali metal surface. This success encourages us to apply our methodology to surface photochemistry.

Key words: alkali-metal surface; chemiluminescence; electron emission; halogen chemisorption; harpooning

Introduction

The chemistry and physics of surface-molecule interactions and reactions are of much interest from both scientific and industrial points of view. Since the system involves the interactions between finite and infinite systems, models are necessary for theoretical investigations of these systems. The results of the investigation are largely dependent upon the nature and the quality of the model adopted. We, therefore, have to carefully examine the models for surface-molecule interactions and reactions.

Quantum chemical models and methods for studying surface-molecule electronic processes should be able to describe the following points. (1) Locality of surface-molecule interactions; (2) effect of bulk solid; (3) electron transfer between adsorbate and surface; (4) surface-adsorbate electrostatic interaction; (5) importance of electron correlations; (6) importance of several lower surface states (ground, excited, and electron-transferred states); (7) roles of photons; (8) surface geometrical structures and reconstructions; (9) interaction between adsorbates (direct and indirect).

The cluster model (CM) has been most frequently used by quantum chemists for investigating chemisorptions and catalytic reactions on metal and semi-conductor surfaces. However, as a model of surface reactions, this model

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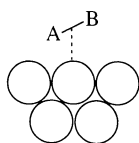
has a defect in that it neglects point (2), the effect of bulk solid. To include such an effect, Grimley, Pisani, and others proposed the embedded cluster model [1-4] and Nakatsuji the dipped adcluster model [5,6].

Figure 1 is a sketch of the concepts of the embedded cluster model (ECM) and the dipped adcluster model (DAM) in comparison with the CM. We define the combined system of admolecule plus cluster as "adcluster". The CM is the free adcluster model. In the ECM, the cluster part of the adcluster is "embedded" in the shaded cluster of atoms which are thought to represent the bulk. The direct interaction between the admolecule and the shaded part is neglected, but its effect is effectively taken into account using Green's function formalism. On the other hand, in the DAM, the adcluster is dipped into the electron bath of the solid and is permitted to achieve equilibrium for electron exchange. This equilibrium is governed by the chemical potentials of the adcluster and the solid.

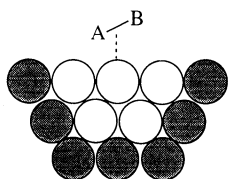
When electron transfer occurs between adsorbate and surface, the electrostatic interaction between them, point (4), becomes important. On a metal surface, this effect appears as an image force. Such electrostatic effects are included in the DAM [5,6].

How do we model a surface ?

Cluster model



Embedded cluster model



Dipped adcluster model

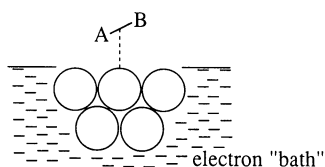


Fig. 1. Illustration of cluster model (CM), embedded cluster model (ECM) and dipped adcluster model (DAM).

Electron correlations are very important since we are mostly interested in systems involving transition metals. Since a surface has many dangling bonds, it usually has several lower excited states. Further, the catalytically active state is not necessarily the ground state but can be an excited state [7], so that our theory should be able to deal with both ground and excited states to the same degree of accuracy. Moreover, electron transfer is sometimes of crucial importance for surface electronic processes and therefore should be described accurately.

The SAC (symmetry adapted cluster)/SAC-CI method [8,9] is useful for studying such systems. Its accuracy and usefulness have been shown through many applications to molecular spectroscopy and excited-state chemistry [10]. When the DAM is combined with the SAC-CI method, we can further deal with points (5), (6), and (7). For example, several adsorbate states like superoxide, peroxide, and atomic oxygen are observed on a surface and they are actually the surface ground and excited states [11]. The remaining points, (8) and (9), are considered when the size of the model is large enough, but become a bottleneck when the number of computations becomes too great. Methods for periodic systems are sometimes useful.

Here, we give a brief review on our recent *ab initio* theoretical studies on surface-molecule interactions and reactions. Explanations are given for our methods of approach to surface-molecule electronic processes and applications are given for halogen chemisorptions on alkali metal surfaces which involve "harpooning" electron transfer, surface chemiluminescence, and surface electron emission. A theoretical study on the high coordination Si, Ge, and Sn complexes in the allylation reaction of formaldehyde will appear [12]. A review of our earlier studies on the catalytic reactions on metal and semiconductor surfaces has been published recently [13].

Dipped adcluster model (DAM)

For surface-molecule interacting systems in which electron transfer between surface and admolecule is important, the CM and the ECM are insufficient, as the cluster size is not large enough. This is because the cluster itself must supply or accommodate electrons by strongly affecting the bonds within the cluster if the cluster is small. In actual metal surfaces, a sufficient number of electrons are involved in extended orbitals, so that the transfer of electrons to or from the admolecule does not significantly affect the local bonding nature of the metal atoms of the cluster directly interacting with the admolecule. There are many cases in which the 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, N₂, etc. The dipped adcluster model (DAM) [5,6] has been proposed for dealing with such sys-

tems. This model has been applied to O_2 chemisorption on palladium [5,6] and silver [11] surfaces.

Figure 2 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 permit an equilibrium to be established for the electron and/or spin transfer between them. The equilibrium would be established when the chemical potential of the adcluster becomes equal to the chemical potential of the surface, or more precisely when the adcluster reaches at the min [$E(n)$] in the range of

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

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, light, etc., are included by variations in the chemical potential μ .

Some typical behavior of the $E(n)$ curve is illustrated in Fig. 3. In case A, the gradient becomes $-\mu$ at $n=n_0$. The $E(n)$ curve is a lower convex for A-1, but an upper convex for A-2. For A-1, the electrons flow into the adcluster up to n_0 , as eqn. (1) implies, since the potential of the adcluster is lower than that of the electron of the metal. The energy of the adcluster is $E(n_0)$. For A-2, 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 electrons flow into it up to i , as eqn. (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 for A-2, transfer of an *integral* number of electrons naturally results so that A-2 is, in some senses, quantum. For case B, there is a region of n where $E(n)$ is lower than $E(0)$, but

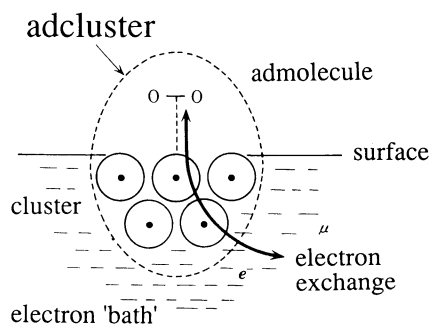


Fig. 2. Concept of the dipped adcluster model (DAM).

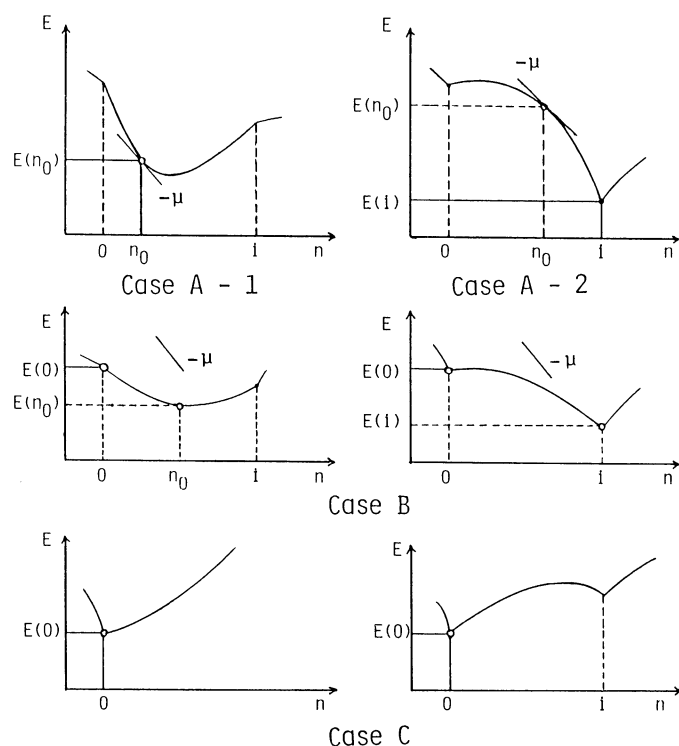


Fig. 3. Typical behavior of the $E(n)$ curve as a function of n , the number of electrons transferred into the adcluster. On the horizontal axis, i denotes an integer number of electrons. The gradient μ is the chemical potential of the metal surface.

the gradient is smaller than μ in that region, so that electron flow does not occur. A device for lowering μ is necessary for electron transfer to occur: a kind of catalyst design. For case C, $E(0)$ is stable in a wide region of n . In this case, electron transfer cannot be expected and the cluster model is appropriate.

Molecular orbital model of the dipped adcluster

We explain the molecular orbital model of the dipped adcluster for calculating the energy $E(n)$ and the electronic structure of the adcluster [5]. We assume that the adcluster exchanges electrons and spins with the solid through its HOMO (highest occupied molecular orbital), LUMO (lowest unoccupied molecular orbital), SOMO (singly occupied molecular orbital), or some other active MO, with the other MOs being doubly occupied or completely unoccupied. Such an active MO is denoted by m . Two types of spin coupling are assumed for the electrons occupying the m th MO. One is called *highest spin coupling*, in which the m th MO is first occupied by an α spin electron and after its occupation becomes unity, it is then occupied by a β spin electron. In this case, the adcluster is paramagnetic. The other is *paired spin coupling* in which

the same numbers of α and β spin electrons occupy the m th MO. Here, the adcluster is always diamagnetic. The energy of the adcluster with n electrons occupying the m th MO, which is assumed to be non-degenerate, is given by

$$E^{(0)} = 2 \sum_k H_k + \sum_{k,l} (2J_{kl} - K_{kl}) + n \sum_k (2J_{km} - K_{km}) + nH_m + Q \quad (2)$$

where k, l run over the doubly occupied MO's. H_k, J_{kl} and K_{kl} denote the core-hamiltonian, coulomb repulsion, and exchange repulsion integrals, respectively. The superscript (0) on E means that it is the energy of the adcluster alone. The quantity Q represents the electron repulsion within the active orbital m . It depends on the nature of the spin coupling and is given by

$$Q = \|n-1\| J_{mm} \quad (3)$$

for the highest spin coupling and

$$Q = \left(\frac{n}{2}\right)^2 J_{mm} \quad (4)$$

for the paired spin coupling. Here, $\|a\| = 0$ if $a < 0$, $\|a\| = a$ if $0 \leq a \leq 1$, and $\|a\| = 1$ if $a > 1$. It is easy to prove that Q is a minimum for the highest spin coupling and maximum for the paired spin coupling. Therefore, the energy of the adcluster itself is lowest for the highest spin coupling. The actual preference of the type of spin coupling would also depend on the nature of the solid and the nature of the interaction between the adcluster and solid. For example, when some amount of α spin is transferred from the solid metal to the adcluster, the system is spin polarized and paramagnetic near the adcluster. For cases in which the orbital m is degenerate, see ref. 5.

The energy of the open-shell restricted Hartree-Fock (RHF) method is written as

$$E = \sum_k \lambda_k H_k + \frac{1}{2} \sum_k \sum_l \lambda_k \lambda_l (\alpha_{kl} J_{kl} - \beta_{kl} K_{kl}). \quad (5)$$

By comparison between eqns. (5) and (2), the occupation parameters λ_k and the spin coupling parameters α_{kl} and β_{kl} in eqn. (5) are fixed, so that performing the RHF-MO SCF calculations involving the non-integral occupation number n , we obtain the molecular orbitals and the energy $E(n)$.

Electrostatic interaction between admolecule and surface

When an electron is transferred from a surface to an admolecule, the electrostatic interaction between them becomes important. When the energy, $E^{(0)}$, of the adcluster alone is calculated by an *ab initio* method, the electrostatic interaction within the adcluster is already included. We define the electrostatic correction term $E^{(1)}$ as being due to the surface region outside the cluster under consideration. The energy of the system thus becomes,

$$E = E^{(0)} + E^{(1)} \quad (6)$$

where $E^{(0)}$ is the energy of the adcluster alone and $E^{(1)}$ the energy of the electrostatic interaction between the adcluster and the bulk metal. For a metal surface, the so-called image force would occur and its inclusion was described in [6]. For a semi-conductor surface, the interaction should be more localized. Such treatment has been described [5].

SAC/SAC-CI method

The SAC (symmetry adapted cluster) method [8] is the cluster expansion based method for calculating ground state and the SAC-CI method [9] 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 necessary for describing these states and utilize the approximate transferability of electron correlations among these states. The SAC/SAC-CI method is therefore more rapidly convergent than ordinary CI expansion and furthermore it gives directly comparable results for the energies and 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 on molecular spectroscopy and excited state chemistry from our laboratory. We believe that the method is simple and accurate enough to be useful. For more details, we refer to a recent review article [10].

Halogen chemisorption on an alkali metal surface

Halogen chemisorption on an alkali metal surface involves interesting electron transfer processes from the surface to the halogen molecule [14]. 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, surface chemiluminescence and electron emission occur. They are the electron transfer processes from the surface to the molecule accompanied by emissions of a photon and an electron, respectively. Up to three electrons are thus transferred from the surface to the molecule.

We have investigated these electron transfer processes by the dipped adcluster model (DAM) [5,6] and the SAC/SAC-CI method [8–10].

The *ab initio* calculations are performed using the program HONDO7 [15] for the SCF calculations and SAC85 [16] for the SAC/SAC-CI calculations. The basis set for Cl is ECP + (3s3p)/[2s2p] [17] + s, p functions with the exponent 0.049 [18] + d-polarization function with $\zeta=0.514$ [19]. For K and

Rb atoms, we use ECP + (10s5p)/[3s3p] bases [17], and for Na (11s5p)/[4s1p] + two *p* functions with the exponents 0.030 and 0.091 [19].

The alkali metal distance is fixed to that observed for the crystals (Na: 3.7083 Å, K: 4.6185 Å, Rb: 4.95 Å) [20] and the work functions are 2.75 eV for Na, 2.30 eV for K and 2.16 eV for Rb metal [21].

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 [14]. However, 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 [22]. We do not take into account the molecular vibration effect. The alkali metal surface is represented by the two metal atoms dipped into the electron bath of the alkali metal surface as illustrated in Fig. 4. We consider here only potassium surface.

We first examine the cluster model: two potassium atoms interacting with Cl_2 . Figure 5 shows the potential curves of the two lowest states calculated by the SAC/SAC-CI method. The lowest curve represents the interaction between neutral K_2 and Cl_2 : it is repulsive throughout the interaction. The other curve is attractive and corresponds to the electron transferred state from Cl_2 to K_2 , but it is always less stable than the non-transferred ground state. Therefore, from this figure, we cannot expect the occurrence of harpooning. Perhaps

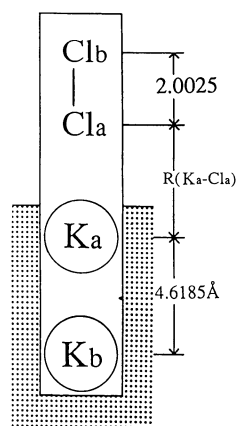


Fig. 4. Model system used for studying “harpooning”.

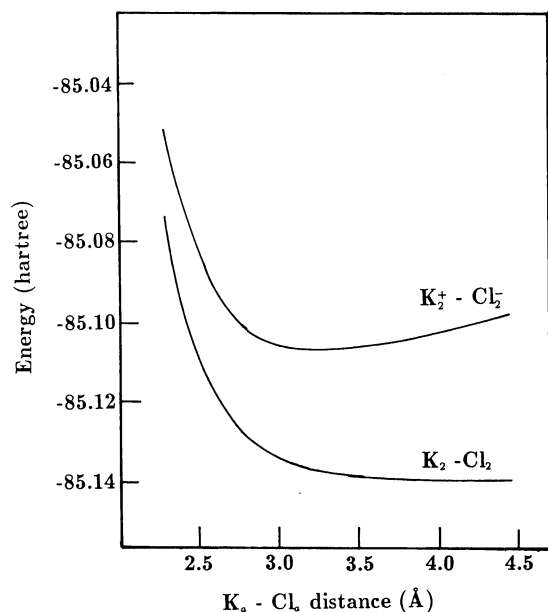


Fig. 5. Potential energy curve for the K_2 - Cl_2 cluster model calculated by the SAC-CI method.

the cluster size is too small to explain the harpooning and furthermore, the vibrational effect of Cl_2 should necessarily be taken into account.

We next apply the molecular orbital model for the DAM. The adcluster, K_2 interacting with Cl_2 , is dipped into the electron bath of the potassium metal whose chemical potential μ is 2.30 eV. Figure 6 shows the $E(n)$ curves, calculated at different separations of Cl_2 from the surface. The curve is calculated by the paired spin coupling model and the highest spin coupling model and the active orbital is chosen to be the σ^* MO of Cl_2 . In the paired spin coupling model, the energy of the system increases with increasing n , so that there is no place at which the tangent of the $E(n)$ curve becomes equal to $-\mu$. However, in the highest spin coupling model, the $E(n)$ curve is an upper convex and its tangent can become larger (in absolute terms) than $-\mu$ when the Cl_a - K_a distance is smaller than 7 Å. Since the $E(n)$ curve is an upper convex, this means that one electron (an integral number, 1) is transferred from the surface to Cl_2 , as explained in the previous section using Fig. 3. 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 vibronic coupling. We also use the picture of "tunneling" from a point on the $E(n)$ curve at $n=0$ to the point at which the derivative $-\partial E/\partial n$ is equal to μ , since between these points the derivative is always less than μ . However, this concept of "tunneling" on the n -space is different from that on the R -space.

Similar results were also obtained from the sodium- Cl_2 and rubidium- Cl_2

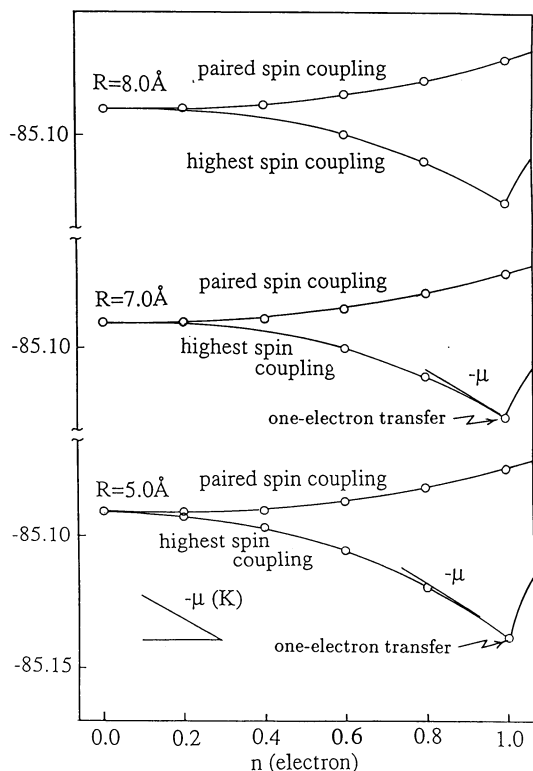


Fig. 6. $E(n)$ curves calculated by the DAM for the Cl_2 -potassium surface system at the K_a - Cl_a distances of 8, 7, and 5 Å.

systems. In summary, the harpooning in the DAM picture is the Franck-Condon one-electron transfer process from the bulk alkali metal to Cl_2 in the highest-spin coupling mechanism. The harpooning distances calculated by DAM are 6, 7, and 8 Å for Na, K, and Rb surfaces, respectively. These distances are shorter than those estimated by the conventional tunneling mechanism, for example, it is estimated to be 10 Å for the Na surface [14].

Elongation and chemisorption of Cl_2^-

When harpooning occurs, Cl_2 becomes Cl_2^- and the Cl-Cl distance increases. Figure 7 shows the potential curve as a function of the Cl-Cl distance of the adcluster, K_2 - Cl_2^- , with the fixed K_a - Cl_a distance of 7.0 Å, the distance at which the harpooning begins to occur. It was calculated by the Hartree-Fock method. Harpooning occurs at the Cl-Cl distance of 2.0025 Å shown by an arrow, as a Franck-Condon process, and afterwards, the Cl-Cl distance is elongated with much stabilization, about 48 kcal/mol, to a Cl-Cl distance of 2.64 Å. The binding energy of Cl_2^- on the surface is calculated to be only 7

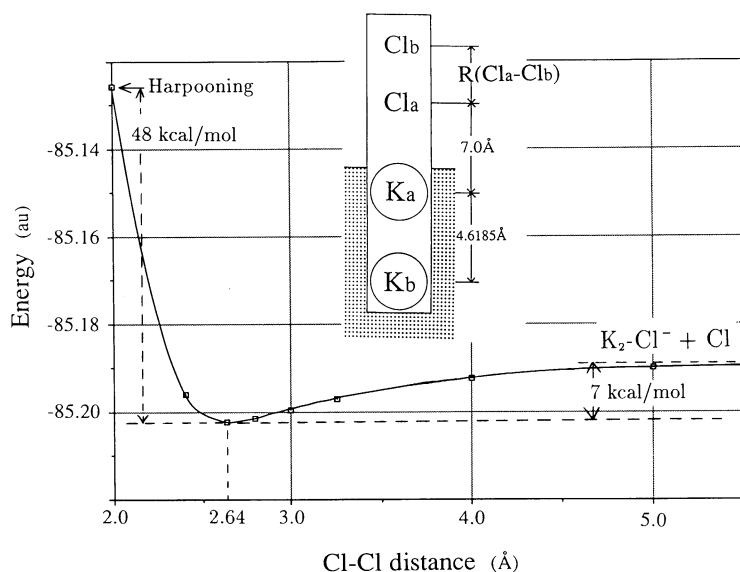


Fig. 7. Potential curve of the adcluster in the Hartree-Fock level as a function of the Cl-Cl distance just after harpooning. The K_a - Cl_a distance is fixed at 7.0 Å.

kcal/mol, which is very small even in comparison with the experimental binding energy, 29 kcal/mol of the free Cl_2^- [22]. Since the energy gain by the elongation ≈ 48 kcal/mol is much larger than the binding energy 7 kcal/mol, we expect that a neutral Cl atom is ejected out from the surface after harpooning.

We assume that this excess energy is dissipated somewhere, probably on the alkali metal surface and calculate the adiabatic potential curve of Cl_2^- on the surface. The potential curve shown in Fig. 8 is calculated for the $K_2-Cl_2^-$ adcluster as a function of the K_a-Cl_a distance: the Cl-Cl distance is optimized at each K_a-Cl_a distance. Starting from the K_a-Cl_a distance of 7 Å, the potential curve is attractive, and the minimum is obtained at the K_a-Cl_a distance of 3 Å. The stabilization energy there is about 27 kcal/mol.

The gross charge of the adcluster at the minimum of the potential shown in Fig. 7 is Cl_b (-0.423), Cl_a (-0.578), K_a (+0.078) and K_b (-0.077). One electron transferred from the bulk metal lies almost entirely on Cl_2 and the potassium atoms of the adcluster are almost neutral. The charge polarization in Cl_2 and K_2 is reasonable in terms of image force. On the other hand, the gross charge at the minimum of Fig. 8 is Cl_b (-0.067), Cl_a (-0.875), K_a (+0.141), and K_b (-0.199): the charge polarization increases greatly.

Surface chemiluminescence process

We next study the surface chemiluminescence process. A second electron is transferred from the metal surface to the halogen molecule with an emission of a photon. Here we take the reaction pathway of the adcluster $K_2-Cl_2^-$ as shown in Fig. 9. The reaction is assumed to proceed from the end-on geometry

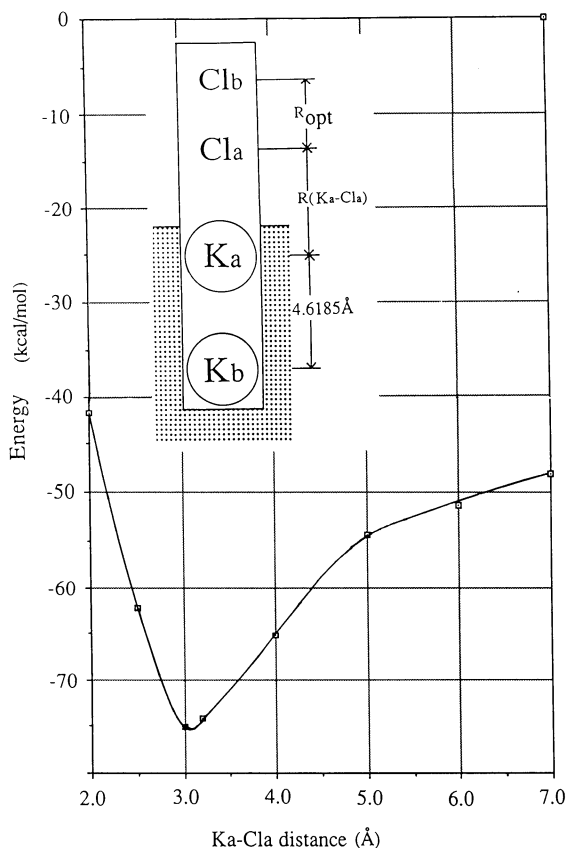


Fig. 8. Potential curve of the adcluster in the Hartree-Fock level as a function of the K_a - Cl_a distance. The Cl-Cl distance is optimized at each K_a - Cl_a distance. The energy is relative to the energy of the system just after harpooning shown by the arrow in Fig. 7 (Cl-Cl distance is 2.0025 Å).

on K_a , #1 and #2 positions, to the dissociated chemisorption structures, #8 and #9 positions. The Cl_a - K_a distance is 3.0 Å for #2 to #8, 3.25 Å for #1 and 2.5 Å for #9. The Cl_a - Cl_b distance at #1 and #2 is 2.73 Å.

An interesting question invoked here is, "from where does the second electron originate?" Does it originate from the bulk metal or from the local K_2 site directly interacting with Cl_2 ? In order to investigate this problem, we calculate by the SAC/SAC-CI method the total energies of the adclusters with the formal charges of $K_2-Cl_2^-$ and $K_2^+-Cl_2^-$, 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 for the geometries #2 to #8. 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 $K_2-Cl_2^-$ adcluster (initial state) and the $K_2^+-Cl_2^-$ adcluster (final state) by the SAC-CI method. Figure 10

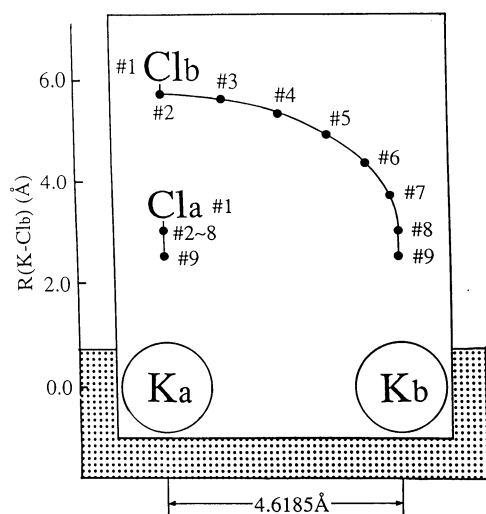


Fig. 9. Assumed reaction pathway for the surface chemiluminescence and surface electron emission processes.

shows the result. The final state is denoted by “chemiluminescence”. It 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 the big arrow, and makes a transition to the chemiluminescence final state by emitting a photon. The energy of the emitted photon is given by the energy difference of the initial and final states plus some part of the kinetic energy of the accelerated Cl_2^- in the initial state. The wave numbers shown in the figure correspond to the former one. Before position #5, only the chemiluminescence transition occurs, but after that, two channels of transitions exist, namely, the chemiluminescence channel and the electron emission channel. The experimentally observed surface chemiluminescence spectrum is shown in Fig. 11 [23]. Experimentally, the spectrum spreads from about 800 nm to 300 nm with the peak maximum at about 440 nm. 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 geometry #5 facilitates this transition. From Fig. 10 we see that the transition occurs mainly at geometries #3 to #6 of the reaction path (Fig. 9): the transition occurs in the course of the dissociative chemisorption. The calculated transition probability has a maximum at geometry #3, while the experimental peak occurs between geometries #4 and #5. This shift is probably due to an addition of the kinetic energy of Cl_2^- to the energy of the emitted photon.

The surface chemiluminescence process is certainly a charge transfer process from the surface to the halogen molecule. The gross charge at geometry #4 is $\text{Cl}_b(-0.158)$, $\text{Cl}_a(-0.778)$, $\text{K}_a(-0.017)$, $\text{K}_b(-0.047)$ in the initial state and $\text{Cl}_b(-0.996)$, $\text{Cl}_a(-0.947)$, $\text{K}_a(+0.737)$, $\text{K}_b(+0.206)$ in the final state.

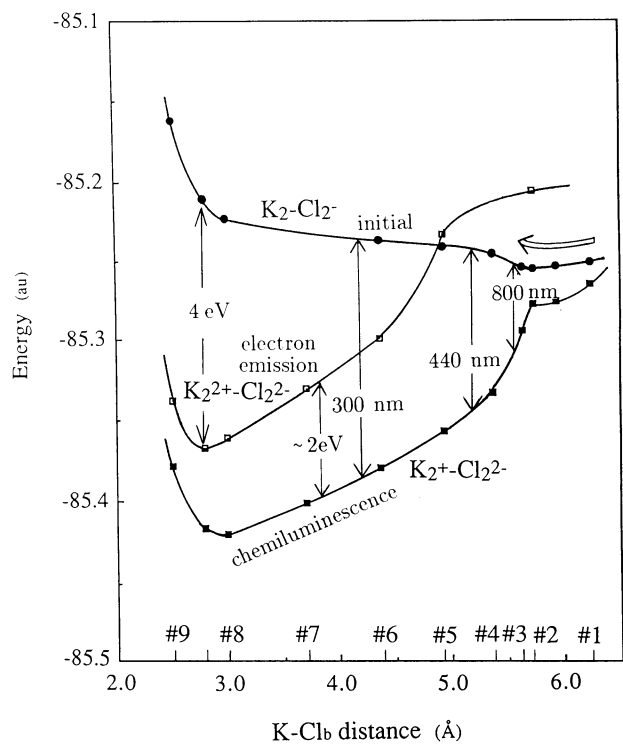


Fig. 10. Potential curves of the Cl_2 -potassium surface system for the surface chemiluminescence and electron emission processes calculated by the SAC/SAC-CI method.

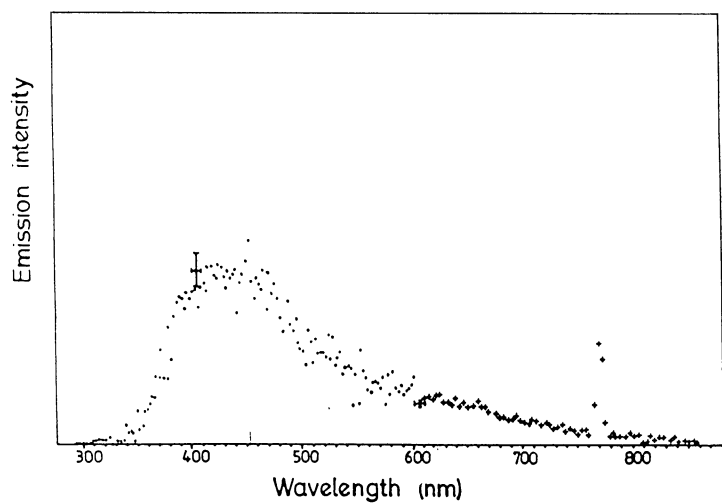


Fig. 11. Observed surface chemiluminescence spectrum for the Cl_2 -potassium surface system (cited from ref. 23).

Surface electron emission process

We consider here 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 X_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 electron bath of the bulk metal. We use the same reaction path as that used for the chemiluminescence process shown in Fig. 9.

Figure 10 also 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 than the chemiluminescence process, since the process proceeds from the right-hand side of the initial-state curve. The emission occurs in the geometries whose numberings are larger than #5, where the initial and final state curves of the electron emission cross each other. The excess (kinetic) energy of the emitted electron is given by the energy difference between the initial and final states plus some part of the kinetic energy of the initial state. The former is about 4 eV at the turning point of the initial state curve, namely at about geometries #8 to #9, where the equilibrium geometry of the final state also exists: prod-

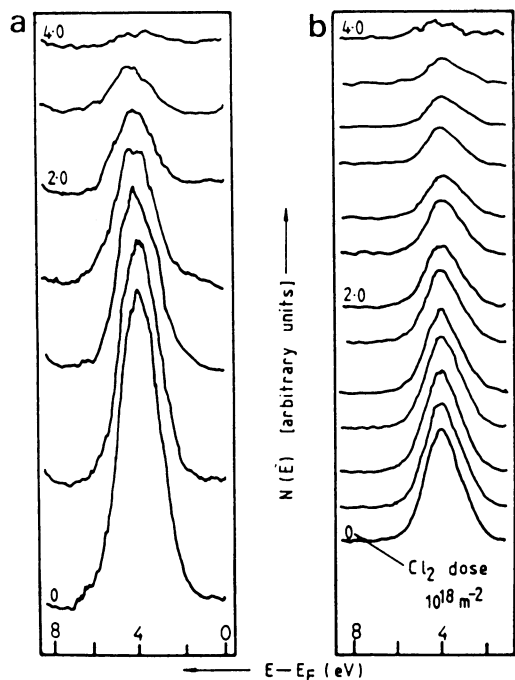


Fig. 12. Exoelectron energy distribution measured for (a) Cl_2 on yttrium and (b) Cl_2 on Rb-dosed yttrium (cited from ref. 24).

uct KCl geometry. We therefore expect a large transition probability at geometries #8 to #9 from these features of the potential curves of the initial and final states: the Franck–Condon factor should be large there. A large transition probability is also expected at the crossing point at about geometry #5 and may be calculated by the Landau–Zener model.

Figure 12 shows the exoelectron energy distributions measured for Cl₂ on yttrium and on Rb-dosed yttrium [24]. We see a maximum peak at about 4 eV in accordance with the above expectation.

The final state of the electron emission process is almost the two potassium chloride. The charge distribution at geometry #6 is Cl_b(−0.936), Cl_a(−0.947), K_a(+0.956), and K_b(+0.927).

In Fig. 10, 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.

Conclusion

We have investigated the electron transfer processes and the chemisorption processes of a halogen molecule on an alkali–metal surface with our methodology, the DAM and the SAC-CI method. The results may be summarized as follows.

(1) The harpooning process is explained by the DAM as a Franck–Condon process. It is a one-electron transfer process from the bulk metal to Cl₂ through the highest-spin coupling mechanism. The harpooning distance for the Cl₂ molecule is calculated to be 6 Å, 7 Å, and 8 Å for sodium, potassium, and rubidium surfaces, respectively.

(2) Upon receiving one electron from the surface, the chlorine molecule elongates its bond distance and the charge polarizes so that the Cl atom closer to the surface is more negative. Since the stabilization energy by this elongation is larger than the Cl–Cl bond energy on the surface, an emission of a Cl atom (neutral) is expected after harpooning. The Cl₂[−] is attracted onto the surface with the minimum at about 3 Å from the surface with the stabilization energy of about 27 kcal/mol.

(3) The surface chemiluminescence process involves another one-electron transfer to Cl₂[−] from the local potassium atoms directly interacting with Cl₂[−]: this electron does not originate from the electron bath of the bulk metal. In other words, it is the electron transfer within the adcluster.

(4) Surface electron emission is a two-electron process, one electron being transferred from the surface to the halogen molecule and the other emitted from the surface. Both electrons originate from the local alkali atoms directly interacting with the halogen molecule.

(5) Both of the surface chemiluminescence and electron emission processes are well represented by the SAC/SAC-CI method. Though these processes involve the ground and excited states and the states having different numbers of electrons, this method gives reliable potential curves for all the states involved. The observed surface chemiluminescence spectrum and the excess-energy distribution spectrum of emitted electrons are understood from the present results.

(6) The initial chemisorption state has two channels of relaxation: one is chemiluminescence, and the other electron emission. The system proceeds from the former channel to the latter because crossing between the initial and final states of the electron emission exists in the course of the reaction pathway (at about geometry # 5). The maximum intensity of the excess energy distribution of the emitted electrons occurs approximately at the geometry of the product, namely KCl.

We conclude that the DAM and the SAC-CI method successfully explain the harpooning, chemisorption, surface chemiluminescence and surface electron emission processes in the chlorine molecule-alkali metal surface system. We have chosen this system because it is closely related to the rapidly growing field of surface photochemistry. The success of our methodology for the present system encourages us to apply it to surface photochemistry.

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