Orientation dependence in the dissociative scattering of hydrogen molecules from metal surfaces: Interference of electron waves in the scattering process

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The molecular orientation dependence of the dissociation probability of hydrogen molecules scattered from metal surfaces is investigated. It is assumed that the dissociation of the molecule is induced by an excitation of electron system in the molecule, involving electron transitions from the bonding state of the molecule to the metal substrate and from the metal substrate to the antibonding state of the molecule. The probability distributions are calculated as functions of the released kinetic energy and the final translational energy of the molecule in the cases when the impinging molecule has various orientations. On the basis of the numerical results, it is found that the orientation dependence of the probability distribution appears as a consequence of the self-interference of electron waves transferring between the impinging molecule and the metal substrate. In addition, a good account of the experimental results can be given for the probability distribution as functions of the released kinetic energy and the molecular orientation with respect to the surface normal.

I. INTRODUCTION

Elementary processes of atoms and molecules on solid surfaces such as scattering, adsorption, and desorption are extensively studied. The dynamical nature of the hydrogen on metal system has recently become one of the most attractive topics in the field of surface science and detailed investigations on dissociative adsorption and associative desorption have been carried out. In particular, the dynamics of hydrogen molecules on a potential energy surface (PES) is studied in the range of translational energies up to ~ 1 eV within the Born-Oppenheimer approximation, and remarkable effects induced by molecular internal degrees of freedom, i.e., vibration and rotation, are clarified.[1–10] On the other hand, in the range of translational energies of a few hundred eV, it was found experimentally that hydrogen molecules can be scattered dissociatively by metal surfaces.[11–19] In this high energy range, it is considered that the dissociation of the molecule is induced by an excitation of electron system in the molecule.[13,19] The excitation involves electron transitions from the bonding state of the molecule to the metal substrate and from the metal substrate to the antibonding state of the molecule, i.e., the dissociation of the impinging molecule is dominated by the electron transition between the impinging molecule and the metal substrate.

It is considered that the electron transition probability between the hydrogen molecule and the metal substrate depends on the hybridization energy between the electron orbital on molecular constituent atoms and that on the metal substrate. As shown in Fig. 1, the absolute value of the hybridization energy becomes larger between the orbital located at the molecular constituent atom A_1 (A_2) and the orbital located at the surface position O_1 (O_2) that is closest to A_1 (A_2), as compared with the other surface position (e.g., O_3). Therefore, it can be considered that the electron might

transfer between the molecular constituent atom A_1 (A_2) and the surface position O_1 (O_2) that is closest to A_1 (A_2), dominantly. Then, it is considered that there may be a self-interference of electron waves transferring between the impinging molecule and the metal substrate because of the path difference d between two electron transition paths, l_1 and l_2, as shown in Fig. 1. If the metal electron with the wave vector $\boldsymbol{k}$ transfers to the impinging molecule, the phase difference δ between l_1 and l_2 is equal to $k_x r \sin\theta$ (k_x is the projection of
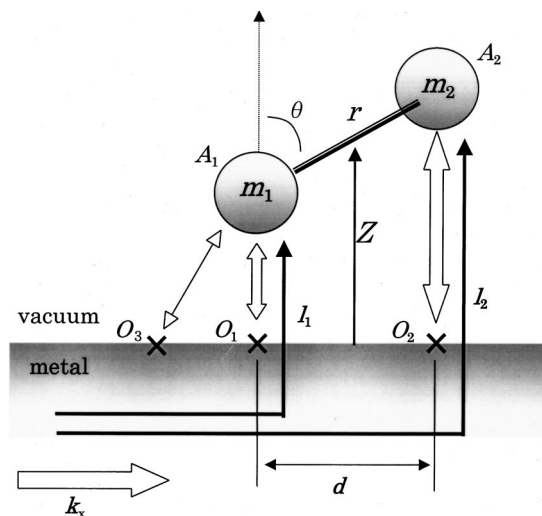

FIG. 1. The model system for a diatomic molecule [two constituent atoms indicated by A_1 and A_2, molecular orientation with respect to the surface normal θ, the distance of center of mass (c.m.) from surface Z, and interatomic distance r] approaching a metal surface. m_1 and m_2 correspond to the masses of the constituent atoms of the diatomic molecule ($M = m_1 + m_2$ in the text). O_1 and O_2 are the surface projections of the two constituent atoms. O_3 is the surface position apart from O_1.
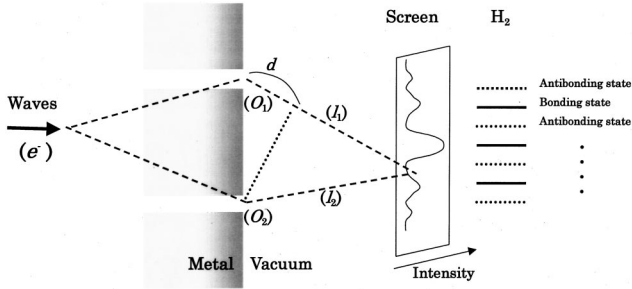
FIG. 2. The typical interference experiment with waves. The surface positions, O_1 and O_2, are analogous to the two holes, and the transitions to the bonding state and the antibonding state of the hydrogen molecule are analogous to increasing and dropping of intensities on the screen.

k in the direction of $\overline{O_1O_2}$, r is the molecular interatomic distance, and θ is the molecular orientation with respect to the surface normal). As mentioned in Sec. III, the electron transition probability between the bonding state of the molecule and the metal substrate is large when $\delta = 0, 2\pi, 4\pi, \ldots$, and the electron transition probability between the antibonding state of the molecule and the metal substrate is large when $\delta = \pi, 3\pi, 5\pi, \ldots$. These conditions are similar to that of the typical interference experiment with waves (one may find out that the surface positions, O_1 and O_2, are analogous to the two holes, and the transitions to the bonding state and the antibonding state of the hydrogen molecule are analogous to increasing and dropping of intensities on the screen, as shown in Fig. 2). So, the hydrogen molecule and the metal substrate behave as the electron wave interferometer.

In previous studies,[19–21] we have investigated the molecular orientation dependence of the probability distribution for the dissociative scattering of hydrogen molecules from metal surfaces, taking account of the coupling between the molecular center-of-mass (c.m.) motion and degrees of freedom of metal electron system, while the molecular interatomic distance is fixed at its equilibrium distance, for simplicity. It has been shown that either a perpendicular orientation or a parallel orientation of the molecule with respect to the surface normal will be preferred in the dissociative scattering, depending on the characteristics and initial states of the reaction partners involved.[19] Moreover, we have investigated how the Coulomb interaction between electrons in the metal substrate has an influence on the molecular orientation dependence of the probability distribution for the dissociative scattering as a function of the final translational energy.[20] We have shown that as the magnitude of the Coulomb interaction in the metal substrate is increased, the probability distribution for the dissociative scattering of the hydrogen molecule increases in the high energy region, where the tail structure of the probability distribution shows up. It was also shown that in the case that the filled-band width is 4 eV [which is related to that of the d band in Cu (Refs. 22 and 23)], at the main peak of the probability distribution, an orientation dependence with a near-perpendicular orientation preference can be seen whether we take into account the Coulomb interaction between electrons in the metal substrate or not. On the other hand, at the high energy tail showing up as the magnitude of the Coulomb interaction is increased, an orien-

tation dependence with a parallel orientation preference can be seen. It is found that these orientation preferences of the probability distribution for the dissociative scattering depend on the wave numbers of electrons involved in the process.

In this study, the probability distributions for dissociative scattering are calculated as functions of the released kinetic energy and the final translational energy of the molecule, further taking account of the relative motion of the molecular nuclei (vibrational motion), because the molecular interatomic distance is the factor that determines the phase difference δ and it is considered that it has an influence on the dissociation probability of the hydrogen molecule. On the basis of numerical results, it is found that the molecular orientation dependence of the probability distributions appears as a consequence of the self-interference of electron waves transferring between the impinging molecule and the metal substrate, and it varies depending on the molecular interatomic distance. In addition, a good account of the experimental results can be given for the probability distribution as functions of the released kinetic energy and the molecular orientation with respect to the surface normal.[13,16]

II. MODEL

A. Hamiltonian

The Hamiltonian for the dissociative scattering of a hydrogen molecule from a metal surface can be expressed as a sum of the Hamiltonians for the electron system in the metal substrate H_S, the impinging molecule, H_M, and the molecule-substrate interaction, $H_{M\text{-}S}$, i.e., $H = H_S + H_M + H_{M\text{-}S}$. In this paper, it is assumed that the electron transfers between the orbitals located at molecular constituent atoms, A_1 and A_2, and those located at surface positions, O_1 and O_2, that are closest to the atoms, A_1 and A_2 (see Fig. 1). Then the Hamiltonian corresponding to the molecule-substrate interaction, $H_{M\text{-}S}$, can be described as

$$H_{M\text{-}S} = \sum_\sigma \left[V_1(Z,\theta) a_{1\sigma}^\dagger C_{O_1\sigma} + V_2(Z,\theta) a_{2\sigma}^\dagger C_{O_2\sigma} + \text{H.c.} \right],$$

$$(1)$$

where

$$C_{O_1\sigma} = \frac{1}{\sqrt{N}} \sum_k C_{k\sigma} \exp\left(i\mathbf{k} \cdot \frac{\mathbf{r}}{2}\sin\theta \right),$$

$$C_{O_2\sigma} = \frac{1}{\sqrt{N}} \sum_k C_{k\sigma} \exp\left(-i\mathbf{k} \cdot \frac{\mathbf{r}}{2}\sin\theta \right). \quad (2)$$

Henceforth, we employ $\hbar = 1$ units. Z is the distance between the molecular center of mass and the surface, and θ is the molecular orientation with respect to the surface normal and may be fixed throughout the scattering processes.[19] $a_{1\sigma}$ ($a_{1\sigma}^\dagger$) and $a_{2\sigma}$ ($a_{2\sigma}^\dagger$) are the single electron annihilation (creation) operators with spin σ in the orbitals, ϕ_1 and ϕ_2, located at atoms A_1 and A_2, respectively. It is noted that these two orbitals, ϕ_1 and ϕ_2, are modified from the $1s$ orbitals of two hydrogen atoms, ψ_1^{1s} and ψ_2^{1s}, such that they are orthogonal to each other.[24] $C_{O_1\sigma}$ ($C_{O_1\sigma}^\dagger$) and $C_{O_2\sigma}$ ($C_{O_2\sigma}^\dagger$) are the single electron annihilation (creation) opera-

tors with spin σ in the orbitals, ϕ_{O_1} and ϕ_{O_2}, located at two surface positions, O_1 and O_2, which are closest to atoms A_1 and A_2, respectively. $C_{k\sigma}$ ($C_{k\sigma}^\dagger$) is the single electron annihilation (creation) operator with the wave vector k and spin σ in the conduction band of the metal substrate. r is the molecular interatomic distance. ϕ_{O_1} and ϕ_{O_2} are expanded in terms of the wave function of an electron with the wave vector k, ϕ_k, multiplied by the phase factor, $\exp[\pm i k \cdot (r/2)\sin\theta]$. The hybridization energy is assumed to have exponential forms

$$V_1(Z,\theta)=V_0 u(Z), \quad V_2(Z,\theta)=V_1(Z,\theta)\exp(-\gamma r\cos\theta), \tag{3}$$

where $u(Z)=\exp(-\gamma|Z|)$. Here, the positive Z region corresponds to the path when the impinging molecule approaches the surface and the negative Z region to the path when the resulting products of the reaction scatter back.[19]

In the free electron approximation, the Hamiltonian of the metal substrate H_S is given by

$$H_S=\sum_{k\sigma} \varepsilon_k C_{k\sigma}^\dagger C_{k\sigma}, \tag{4}$$

where ε_k is the kinetic energy of an electron in the conduction band of the metal substrate. The Hamiltonian for the impinging molecule is separated into that for the c.m. motion $H_{\text{c.m.}}$, for the relative motion of the molecular nuclei H_{REL}, and for electrons of the impinging molecule H_E, i.e., $H_M=H_{\text{c.m.}}+H_{REL}+H_E$, where

$$H_{\text{c.m.}}=-\frac{1}{2M}\frac{\partial^2}{\partial Z^2}, \quad H_{REL}=-\frac{1}{2\mu}\frac{\partial^2}{\partial r^2}+\frac{1}{r}. \tag{5}$$

M is the total mass of the molecule, and μ is the reduced mass of the molecule. The Hamiltonian for electrons of the impinging molecule, H_E, is assumed as

$$H_E=\sum_\sigma \varepsilon_a(r)(n_{a1\sigma}+n_{a2\sigma})+t(r)\sum_\sigma (a_{1\sigma}^\dagger a_{2\sigma}+\text{H.c.})$$
$$+U_a(r)(n_{a1\uparrow}n_{a1\downarrow}+n_{a2\uparrow}n_{a2\downarrow})+J(r)\sum_{\sigma,\sigma'} n_{a1\sigma}n_{a2\sigma'}, \tag{6}$$

where $\varepsilon_a(r)$ is the energy of an electron in the orbitals ϕ_1 and ϕ_2, $t(r)$ is the hybridization energy between the two orbitals ϕ_1 and ϕ_2, $U_a(r)$ and $J(r)$ are the intra-atomic and interatomic Coulomb interaction energies, and $n_{ai\sigma}=a_{i\sigma}^\dagger a_{i\sigma}$. Explicit expressions for $\varepsilon_a(r)$, $t(r)$, $U_a(r)$, and $J(r)$ are given in Ref. 24 with their dependence on the molecular interatomic distance r.

B. The wave functions

Using the model Hamiltonian described above, the dissociation probability of a hydrogen molecule scattering from a metal surface into two neutral hydrogen atoms is calculated. It is assumed that the dissociation is triggered/induced by a following two-step process. Initially, (1) one of the electrons in the bonding orbital of the impinging molecule transfers to an unoccupied state in the metal substrate, and (2) an elec-

tron from an occupied state in the metal substrate transfers to the antibonding orbital, or process (2) occurs and then (1). The corresponding total wave functions for the initial and final states, $|\Phi_i\rangle$ and $|\Phi_f\rangle$, are given by

$$|\Phi_i\rangle=|\Lambda_i\rangle|K_i\rangle|0\rangle \tag{7}$$

and

$$|\Phi_f\rangle=|\Lambda_f\rangle|K_f\rangle|E\rangle, \tag{8}$$

respectively. $|\Lambda_i\rangle$ and $|\Lambda_f\rangle$ are the initial and final states of the total electron system in the molecule and the metal substrate;

$$|\Lambda_i\rangle=\frac{1}{\sqrt{2}}[\chi_b(r)C_{b\uparrow}^\dagger C_{b\downarrow}^\dagger-\chi_a(r)C_{a\uparrow}^\dagger C_{a\downarrow}^\dagger]|F\rangle \tag{9}$$

and

$$|\Lambda_f\rangle\simeq\frac{1}{\sqrt{3}}\Big[C_{a\downarrow}^\dagger C_{b\downarrow}^\dagger C_{k'\downarrow}C_{k\uparrow}^\dagger-C_{a\uparrow}^\dagger C_{b\uparrow}^\dagger C_{k'\uparrow}C_{k\downarrow}^\dagger$$
$$+\frac{1}{2}(C_{a\uparrow}^\dagger C_{b\downarrow}^\dagger+C_{a\downarrow}^\dagger C_{b\uparrow}^\dagger)(C_{k'\uparrow}C_{k\uparrow}^\dagger-C_{k'\downarrow}C_{k\downarrow}^\dagger)\Big]|F\rangle. \tag{10}$$

The Heitler-London wave function is used for the initial wave function for the electron system of the impinging molecule (cf. Ref. 25). $|F\rangle$ is the wave function for the electron system of the substrate in the initial state. $\chi_b(r)$ and $\chi_a(r)$ are given by

$$\chi_b(r)=\frac{1+S(r)}{\sqrt{1+S(r)^2}}, \quad \chi_a(r)=\frac{1-S(r)}{\sqrt{1+S(r)^2}}, \tag{11}$$

where $S(r)$ is the overlap integral between the $1s$ orbitals of two hydrogen atoms, $\psi_1^{1S}(x)$ and $\psi_2^{1S}(x)$:[25]

$$S(r)=\int dx\, \psi_1^{1S*}(x)\psi_2^{1S}(x). \tag{12}$$

$C_{a\sigma}$ ($C_{a\sigma}^\dagger$) and $C_{b\sigma}$ ($C_{b\sigma}^\dagger$) are the single electron annihilation (creation) operators with spin σ in the antibonding and bonding orbitals of the impinging molecule, described as

$$C_{a\sigma}=\frac{1}{\sqrt{2}}(a_{1\sigma}-a_{2\sigma}), \quad C_{b\sigma}=\frac{1}{\sqrt{2}}(a_{1\sigma}+a_{2\sigma}). \tag{13}$$

The eigenfunctions and energy eigenvalues for the relative motion of the molecular nuclei in the initial and the final states obey the Schrödinger equations,

$$[H_{REL}+\varepsilon_{E,i}(r)]|0\rangle=\varepsilon_g|0\rangle \tag{14}$$

and

$$[H_{REL}+\varepsilon_{E,f}(r)]|E\rangle=E|E\rangle, \tag{15}$$

where $|0\rangle$ and ε_g are the wave function and the energy for the lowest vibrational state of the molecule when the electronic state is $|\Lambda_i\rangle$. $|E\rangle$ is the wave function for the relative motion of the molecular nuclei with continuous energy ei-
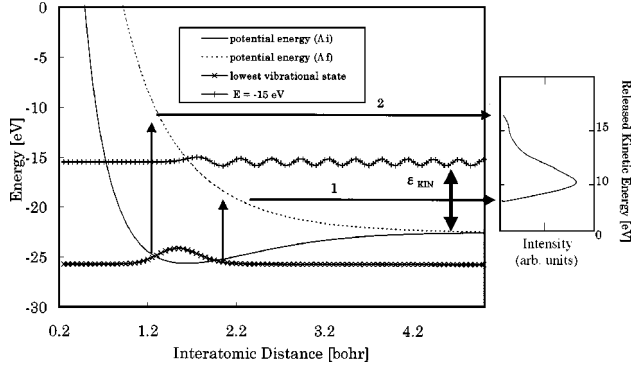
FIG. 3. In the left-hand box, the potential energies for the relative motion of the molecular nuclei are shown as a function of the molecular interatomic distance, and the wave functions for the lowest vibrational state of the molecule when the electronic state is $|\Lambda_i\rangle$ and for the relative motion of the molecular nuclei with continuous energy eigenvalue $E(=-15\text{ eV})$ when the electronic state is $|\Lambda_f\rangle$ are shown as a function of the molecular interatomic distance. The released kinetic energy ε_{KIN} is denoted by the up-and-down arrow. In the right-hand box, an intensity spectrum for the transition between $|\Lambda_i\rangle$ and $|\Lambda_f\rangle$ as a function of the released kinetic energy in the case that the molecular interatomic distance and vibrational motion do not change during the electron transition as a reference.

genvalue E when the electronic state is $|\Lambda_f\rangle$. $\varepsilon_{E,i}(r)$ and $\varepsilon_{E,f}(r)$ are energies of the molecular electron system in the initial and final states,

$$\varepsilon_{E,i}(r)=\chi_b^2(r)[\varepsilon_a(r)+t(r)]+\chi_a^2(r)[\varepsilon_a(r)-t(r)]$$
$$+\frac{\chi_b^2(r)+\chi_a^2(r)}{2}\frac{U_a(r)+J(r)}{2}$$
$$-\chi_b(r)\chi_a(r)\frac{U_a(r)-J(r)}{2} \qquad (16)$$

and

$$\varepsilon_{E,f}(r)=2\varepsilon_a(r)+J(r). \qquad (17)$$

The potential energies for the relative motion of the molecular nuclei $\varepsilon_{E,i}(r)+1/r$ and $\varepsilon_{E,f}(r)+1/r$ are shown in Fig. 3. The energy released between the fragments (the released kinetic energy[12,15] ε_{KIN}) is represented by the up-and-down arrow in Fig. 3. It is defined as the difference between the energy E and the lowest dissociation limit $\varepsilon_{E,f}(r\rightarrow\infty)$, i.e.,

$$\varepsilon_{KIN}=E-\varepsilon_{E,f}(r\rightarrow\infty). \qquad (18)$$

$|K_i\rangle$ and $|K_f\rangle$ are the wave functions for the c.m. motion of the impinging molecule in the initial and final states, respectively. A plane wave function is chosen to represent the state of the c.m. motion, i.e., $\langle Z|K\rangle \propto \exp(-iKZ)$, and the c.m. motion energies in the initial and final states, $\varepsilon_{\text{c.m.},i}$ and $\varepsilon_{\text{c.m.},f}$, are given by $K_i^2/2M$ and $K_f^2/2M$, respectively.

C. The expression for the dissociation probability

The expression for the dissociation probability that the impinging molecule and the metal substrate, initially in $|\Phi_i\rangle$, ends up in $|\Phi_f\rangle$ is written as

$$W_D=2\pi\sum_f |\langle\Phi_f|H_{M\text{-}S}(1+G_{TOT}H_{M\text{-}S})|\Phi_i\rangle|^2\delta(E_f-E_i),$$
$$(19)$$

where G_{TOT} is the Green function defined by the total Hamiltonian, $H=H_{CM}+H_{REL}+H_S+H_E+H_{M\text{-}S}$;

$$G_{TOT}=\frac{1}{E_i-H+i\eta} \quad (\eta\rightarrow 0^+). \qquad (20)$$

E_i and E_f are the energies in the initial and final states, given by

$$E_i=2\sum_{|l|\le k_F}\varepsilon_l+\varepsilon_{\text{c.m.},i}+\varepsilon_g \qquad (21)$$

and

$$E_f=2\sum_{|l|\le k_F}\varepsilon_l+\varepsilon_k-\varepsilon_{k'}+\varepsilon_{\text{c.m.},f}+E. \qquad (22)$$

We define the Green function g by the Hamiltonian for the molecular c.m. motion, $H_{\text{c.m.}}$, and the electron system, H_S, H_E, and $H_{M\text{-}S}$, i.e.,

$$g=\frac{1}{\varepsilon_{S,i}+\varepsilon_{\text{c.m.},i}+\varepsilon_{E,i}-(H_S+H_{\text{c.m.}}+H_E+H_{M\text{-}S})+i\eta},$$
$$(23)$$

and G_{TOT} is described as the expansion in terms of $\varepsilon_{REL,i}-H_{REL}$,

$$G_{TOT}=g+g(\varepsilon_{REL,i}-H_{REL})g+g(\varepsilon_{REL,i}-H_{REL})g(\varepsilon_{REL,i}-H_{REL})g+\cdots. \qquad (24)$$

Here, we take into account the first term, which leads to the Born-Oppenheimer approximation,[26] and g is expanded in terms of the perturbation Hamiltonian $H_{M\text{-}S}$. Finally, G_{TOT} becomes

$$G_{TOT}\simeq G_0+G_0 H_{M\text{-}S}G_0+G_0 H_{M\text{-}S}G_0 H_{M\text{-}S}G_0+\cdots, \qquad (25)$$

where G_0 is the unperturbed Green function, defined by the Hamiltonian of the unperturbed system, $H_0=H_S+H_E+H_{\text{c.m.}}$:

$$G_0=\frac{1}{\varepsilon_{S,i}+\varepsilon_{\text{c.m.},i}+\varepsilon_{E,i}-(H_S+H_{\text{c.m.}}+H_E)+i\eta}. \qquad (26)$$

Using Eq. (25), up to the fourth order in the perturbation Hamiltonian $H_{M\text{-}S}$, the probability distribution for the dissociative scattering from the metal substrate at finite temperatures is written as

$$W_D=\frac{3(V_0 M\gamma)^4}{2K_i K_f}\int d\varepsilon\rho(\varepsilon)\rho(\varepsilon+A)[1-f(\varepsilon)]f(\varepsilon+A)$$
$$\times\int dr_1\langle E|r_1\rangle\langle r_1|0\rangle$$
$$\times\int dr_2\langle E|r_2\rangle\langle r_2|0\rangle F(r_1,r_2,\varepsilon), \qquad (27)$$

where

$$
\begin{aligned}
F(r_1,r_2,\varepsilon) = & \chi_b(r_1)\chi_b(r_2)[X_+(\varepsilon)+Y_+(\varepsilon)][X_+(\varepsilon) \\
& -Y_+(\varepsilon)]T^{(1)}(B_1,B_2,\varepsilon)T^{(2)}(B_1,B_2,\varepsilon)^* \\
& +\chi_a(r_1)\chi_b(r_2)[X_-(\varepsilon)-Y_-(\varepsilon)][X_-(\varepsilon) \\
& +Y_-(\varepsilon)]T^{(1)}(B_3,B_4,\varepsilon)T^{(2)}(B_1,B_2,\varepsilon)^* \\
& +\chi_b(r_1)\chi_a(r_2)[X_-(\varepsilon)+Y_-(\varepsilon)][X_-(\varepsilon) \\
& -Y_-(\varepsilon)]T^{(1)}(B_1,B_2,\varepsilon)T^{(2)}(B_3,B_4,\varepsilon)^* \\
& +\chi_a(r_1)\chi_a(r_2)[X_+(\varepsilon)-Y_+(\varepsilon)][X_+(\varepsilon) \\
& +Y_+(\varepsilon)]T^{(1)}(B_3,B_4,\varepsilon)T^{(2)}(B_3,B_4,\varepsilon)^*.
\end{aligned}
\tag{28}
$$

Here $\rho(\varepsilon)$ is the electron density of states in the metal substrate, $f(\varepsilon)$ is the Fermi distribution function, and A is the difference between the energies of the impinging molecule in the initial and final states, given by

$$
A = \varepsilon_{\mathrm{c.m.},f} - \varepsilon_{\mathrm{c.m.},i} + E - \varepsilon_g.
\tag{29}
$$

$T^{(l)}$ $(l=1,2)$ is the molecular orientation independent term given by

$$
\begin{aligned}
T^{(l)}(\alpha,\beta,\varepsilon) = \sum_p \Bigg[& \frac{\langle K_f|u(Z)|K_p\rangle\langle K_p|u(Z)|K_i\rangle}{\varepsilon_{\mathrm{c.m.},f}-\varepsilon_{\mathrm{c.m.},p}+\varepsilon+\alpha(r_l)+i\eta} \\
& +\frac{\langle K_f|u(Z)|K_p\rangle\langle K_p|u(Z)|K_i\rangle}{\varepsilon_{\mathrm{c.m.},i}-\varepsilon_{\mathrm{c.m.},p}-\varepsilon+\beta(r_l)+i\eta} \Bigg]
\end{aligned}
\tag{30}
$$

and

$$
\begin{aligned}
B_1(r) &= E - \varepsilon_g + \varepsilon_{E,i} - (3\varepsilon_a + t + U + 2J), \\
B_2(r) &= \varepsilon_{E,i} - (\varepsilon_a + t), \\
B_3(r) &= E - \varepsilon_g + \varepsilon_{E,i} - (3\varepsilon_a - t + U + 2J), \\
B_4(r) &= \varepsilon_{E,i} - (\varepsilon_a - t).
\end{aligned}
\tag{31}
$$

$X_\pm$ and $Y_\pm$ are the molecular orientation dependent terms given by

$$
\begin{aligned}
X_\pm(\varepsilon) = 1 \pm & e^{-(r_1+r_2)\gamma\cos\theta} \\
& \times \frac{2\sin\{\sqrt{2(\varepsilon+D)}[(r_1-r_2)/2]\sin\theta\}}{\sqrt{2(\varepsilon+D)}[(r_1-r_2)/2]\sin\theta},
\end{aligned}
\tag{32}
$$

and

$$
\begin{aligned}
Y_\pm(\varepsilon) = & (e^{-r_1\gamma\cos\theta} \pm e^{-r_2\gamma\cos\theta}) \\
& \times \frac{2\sin\{\sqrt{2(\varepsilon+D)}[(r_1+r_2)/2]\sin\theta\}}{\sqrt{2(\varepsilon+D)}[(r_1+r_2)/2]\sin\theta}.
\end{aligned}
\tag{33}
$$

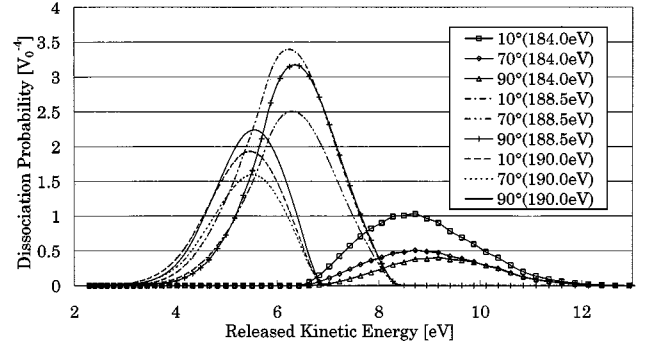D is the value of the filled-band width of the electron system in the metal substrate.

FIG. 4. Dissociation probability as a function of the released kinetic energy ε_{KIN} for molecular orientations, $\theta=10°$, $70°$, and $90°$. We calculate the probability distributions for $\varepsilon_{\mathrm{c.m.},f}$ $=184.0$ eV, 188.5 eV, and 190.0 eV, and the parameter values $\gamma=0.7$ bohr^{-1}, the metal substrate temperature $T_S=500$ K, the filled-band width $D=4$ eV (the value is roughly related to that of the d band in Cu), and $\varepsilon_{\mathrm{c.m.},i}=200$ eV for the impinging molecule. The Fermi level is chosen as the origin of energy.

III. NUMERICAL RESULTS

A. The probability distribution as a function of the released kinetic energy

The probability distributions for the dissociative scattering are calculated in the case when the impinging molecule has an initial orientation $\theta=10°$, $70°$, and $90°$ with respect to the surface normal. The value that is roughly related to that of the d band in Cu is used for the filled-band width D [$=4$ eV (Refs. 22 and 23)] of the metal substrate. The numerical results are shown in the cases when $\varepsilon_{\mathrm{c.m.},f}=184.0$ eV, 188.5 eV, and 190.0 eV as a function of the released kinetic energy of the impinging molecule in Fig. 4.

It is shown in Fig. 4 that in the probability peak when $\varepsilon_{\mathrm{c.m.},f}=184.0$ eV and on the left side of the probability peak when $\varepsilon_{\mathrm{c.m.},f}=188.5$ eV ($\varepsilon_{KIN}\lesssim7$ eV), an orientation dependence of the dissociation probability with a near-perpendicular orientation preference can be seen, and on the right side of the probability peak when $\varepsilon_{\mathrm{c.m.},f}=190.0$ eV($\varepsilon_{KIN}\gtrsim5$ eV), an orientation dependence with a parallel orientation preference can be seen. We can show that the orientation dependence of the probability distribution appears as a consequence of the self-interference of electron waves transferring between the impinging molecule and the metal substrate in the following way.

(1) We calculate the electron transition probability between the antibonding orbital of the impinging molecule and the metal substrate. Up to second order in $H_{M\text{-}S}$, it is found that the electron transition probability is proportional to $\sin^2[\boldsymbol{k}'\cdot(\boldsymbol{r}/2)\sin\theta]$, and that the transition probability becomes large when $\boldsymbol{k}'\cdot(\boldsymbol{r}/2)\sin\theta$ is equal to $(2m+1)\pi/2$, i.e., $\boldsymbol{k}'\cdot\boldsymbol{r}\sin\theta=(2m+1)\pi$, where m is the positive integer. Here, the factor $\boldsymbol{k}'\cdot\boldsymbol{r}\sin\theta$ is the phase difference δ mentioned in Sec. I. We can also calculate the electron transition probability between the bonding orbital of the impinging molecule and the metal substrate in the same way, and it is found that the electron transition probability is proportional to $\cos^2[\boldsymbol{k}\cdot(\boldsymbol{r}/2)\sin\theta]$, and that the transition probability becomes large when $\delta(=\boldsymbol{k}\cdot\boldsymbol{r}\sin\theta)=2m\pi$. That is to say, when phase difference δ is equal to $2m\pi$, the probability of the electron transition between the bonding orbital and the metal
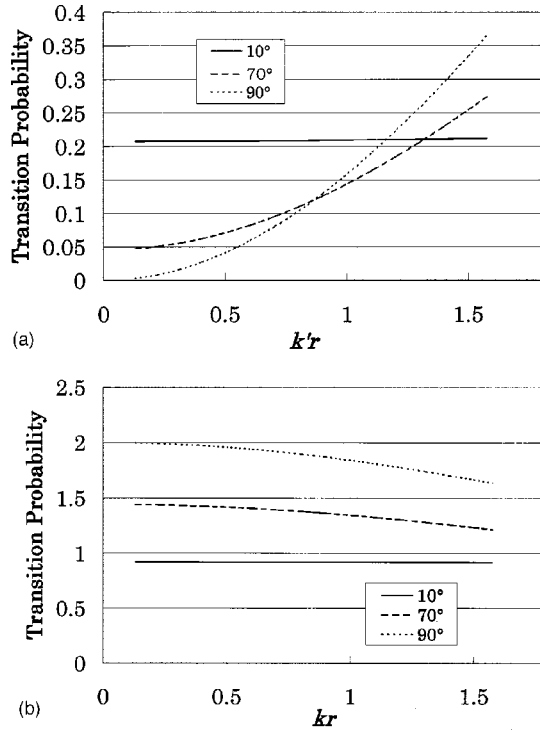
FIG. 5. Transition probability as a function of kr ($k'r$) summing up with respect to the azimuth and the polar angle of k (k'), for molecular orientations, $\theta = 10°$, $70°$, and $90°$ between (a) the antibonding orbital and the metal substrate, and between (b) the bonding orbital and the metal substrate

substrate becomes large, and when δ is equal to $(2m+1)\pi$, the probability of the electron transition between the antibonding orbital and the metal substrate becomes large. These results coincide with those shown in the study of Gadzuk, where he has investigated the orientation dependence of charge transfer into the bonding and antibonding orbitals of a simple diatomic molecule.[27] The transition probabilities can be summed up with respect to the azimuth angle and the polar angle of k (k'). The results in the case when the impinging molecule has an initial orientation $\theta = 10°$, $70°$, and $90°$ are shown as a function of kr ($k'r$) in Figs. 5(a) and 5(b). In the case that the electron transfers between the antibonding orbital and the metal substrate [Fig. 5(a)], it is found that the three curves in the cases of $\theta = 10°$, $70°$, and $90°$ cross around the value of $k'r = 1.2$. When the value of $k'r$ is small ($k'r<1.2$), an orientation dependence of the electron transition probability with a near-perpendicular orientation preference can be seen. On the other hand, when the value of $k'r$ is large ($k'r>1.2$), the orientation dependence with a parallel orientation preference can be seen [labeled orientation dependence (a)]. In the case that the electron transfers between the bonding orbital and the metal substrate [Fig. 5(b)], it is found that in the considerable range of kr ($0 < kr < 1.5$), an orientation dependence of the electron transition probability with a parallel orientation preference can be seen [labeled orientation dependence (b)]. As mentioned in Secs. I and II, it is considered that in the scattering process, the dissociation of the molecule is induced by an excitation of electron system in the molecule involving electron transition from the bonding state of the molecule to the metal substrate and from the metal substrate to the antibonding

state of the molecule. Therefore, the orientation dependence of the probability distribution of the dissociative scattering can be determined by both the orientation dependence (a) and (b). However, it is found that the orientation dependence (a) is dominant because orientation dependence (b) modifies orientation dependence (a) just slightly, and is determined by the wave number k' of the electron transferring from the metal substrate to the antibonding state and the molecular interatomic distance r. As a matter of course, it is important that the amplitude of the wavelength of the electron, $\sim 1/k'$, is comparable to the amplitude of the interatomic distance r for showing the orientation dependence described above.

(2) Under the assumption that the positions and velocities of the molecular nuclei do not change during the electron transition involving an excitation of the electron system in the molecule from the bonding state to the antibonding state (the Franck-Condon principle), the electron transition process indicated by the up arrows in Fig. 3 occurs dominantly, and it is found that as the molecular interatomic distance r is larger, the released kinetic energy ε_{KIN} becomes lower (indicated by the right arrow 1 in Fig. 3), and as r is smaller, ε_{KIN} becomes higher (indicated by right arrow 2).

From methods (1) and (2), we can explain numerical results. When $\varepsilon_{c.m.,f} = 184.0$ eV (located in the high released kinetic energy region; see Fig. 4), the molecular interatomic distance r is small in all of the range of the peak, and the value of $k'r$ is small for any wave numbers k' of the electron transferring between the impinging molecule and the metal substrate ($k'r<1.2$). So, it is found from Fig. 5(a) that the orientation dependence with a near-perpendicular orientation preference can be seen. On the right-hand side of the probability peak, when $\varepsilon_{c.m.,f} = 190.0$ eV (located in the low released kinetic energy region; see Fig. 4), r is large, and the value of $k'r$ is large for any k' ($k'r>1.2$). So, it is found that the orientation dependence with a parallel orientation preference can be seen. On the left-hand side of the probability peak, when $\varepsilon_{c.m.,f} = 190.0$ eV, electrons with small wave number transfer to the molecule, and r is large. So, the value of $k'r$ is almost comparable to that of the curve crossing point (~ 1.2), and there is no difference between the probability distributions in the cases of $\theta = 10°$ and $90°$. On the left-hand side of the probability peak, when $\varepsilon_{c.m.,f} = 188.5$ eV (see Fig. 4), electrons with small wave number transfer to the molecule, and the value of $k'r$ is small for any r ($k'r<1.2$). So, it is found that the orientation dependence with a near-perpendicular orientation preference can be seen. On the right side of the probability peak when $\varepsilon_{c.m.,f} = 188.5$ eV, electrons with large wave number transfer to the molecule, and r is small. So, the orientation preference cannot be seen in the same way as the left-hand side of the probability peak, when $\varepsilon_{c.m.,f} = 190.0$ eV. In this way, the orientation preferences of the probability distributions for the dissociative scattering depend on the molecular interatomic distance and the wave numbers of electrons, i.e., the interference of electron waves transferring between the impinging molecule and the metal substrate has an influence on the orientation dependence of the probability distributions.

B. The probability distribution as a function of the translational energy

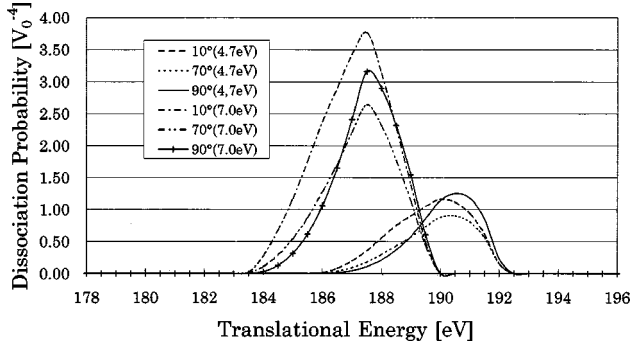The numerical results of the probability distributions for the dissociative scattering are shown in the case when ε_{KIN}

FIG. 6. Dissociation probability as a function of the translational energy $\varepsilon_{c.m.,f}$ for molecular orientations $\theta = 10°$, $70°$, and $90°$. We calculate the probability distributions for $\varepsilon_{KIN} = 4.7$ eV and 7.0 eV and the parameter values $\gamma = 0.7$ bohr^{-1}, the metal substrate temperature $T_S = 500$ K, the filled-band width $D = 4$ eV, and $\varepsilon_{c.m.,i} = 200$ eV for the impinging molecule.

$= 4.7$ eV and 7.0 eV as a function of the final translational energy of the impinging molecule in Fig. 6. It is shown in Fig. 6 that in the probability peak when $\varepsilon_{KIN} = 7.0$ eV, an orientation dependence of the dissociation probability with a near-perpendicular orientation preference can be seen. When $\varepsilon_{KIN} = 7.0$ eV, which corresponds to the high released kinetic energy, the molecular interatomic distance r is small as shown in Fig. 3, and the value of $k'r$ is small for any wave numbers k' of the electron transferring between the impinging molecule and the metal substrate ($k'r < 1.2$). So, it is found from Fig. 5(a) that the orientation dependence of the dissociation probability with a near-perpendicular orientation preference can be seen.

On the left-hand side of the probability peak when $\varepsilon_{KIN} = 4.7$ eV, an orientation dependence of the dissociation probability with a near-perpendicular orientation preference can be seen, because electrons with small wave number transfer to the molecule, and the value of $k'r$ is small for r at $\varepsilon_{KIN} = 4.7$ eV ($k'r < 1.2$). On the right-hand side of the probability peak when $\varepsilon_{KIN} = 4.7$ eV, an orientation dependence with a parallel orientation preference can be seen, because electrons with large wave number transfer to the molecule, and the value of $k'r$ is large for r ($k'r > 1.2$).

C. Electron correlation effects

In this subsection, we investigate how the Coulomb interaction between electrons in the metal substrate has an influence on the molecular orientation dependence as functions of the released kinetic energy and the translational energy. In the case for which the metal substrate has a highly correlated electron system, such as a transition metal substrate, the Hamiltonian for the electron system in the metal substrate H_S is assumed to be described by the Hubbard model,

$$H_S = \sum_{k\sigma} \varepsilon_k C_{k\sigma}^\dagger C_{k\sigma}$$

$$+ \frac{U}{N} \sum_{k_1,k_2,k_3,k_4} C_{k_1\uparrow}^\dagger C_{k_2\downarrow}^\dagger C_{k_3\downarrow} C_{k_4\uparrow} \delta_{k_1+k_2,k_3+k_4},$$

$$(34)$$

where U is the Coulomb interaction between electrons and N is the total number of lattice sites in the substrate. Within the framework of the Hubbard model (34), we can derive the expression of the probability distribution for the dissociative scattering. The expression for the interacting electron system can be produced by replacing the factor $[1 - f(\varepsilon_k)] f(\varepsilon_k + A)$ with $\langle 1 - \tilde{n}(\varepsilon_k) \rangle \langle \tilde{n}(\varepsilon_k + A) \rangle$ and ε_k with $\varepsilon_k + U/2$ in the energy denominator of the expression (30), in the single-site approximation.[20,28] Here, $\langle \tilde{n}(\varepsilon_k) \rangle$ is the occupation probability for an electron in the state of energy ε_k given by

$$\langle \tilde{n}(\varepsilon_k) \rangle = -\frac{1}{\pi} \int_{-\infty}^{\infty} d\varepsilon \, f(\varepsilon) \text{Im}[\langle\langle C_{k\sigma}; C_{k\sigma}^\dagger \rangle\rangle_\varepsilon^R]. \quad (35)$$

where $\langle\langle C_{k\sigma}; C_{k\sigma}^\dagger \rangle\rangle_\varepsilon^R$ is the one particle Green function,

$$\langle\langle C_{k\sigma}; C_{k\sigma}^\dagger \rangle\rangle_\varepsilon^R = \frac{1}{\varepsilon - \varepsilon_k - \Sigma(\varepsilon)}, \quad (36)$$

and $\Sigma(\varepsilon)$ is the self-energy. In order to carry out the numerical calculation of the probability distribution for the dissociative scattering, a second-order perturbation calculation with respect to U is made for the self-energy of a single electron in the metal substrate,[20,28] and the occupation probability for an electron in the state of energy ε_k, $\langle \tilde{n}(\varepsilon_k) \rangle$, can be derived by Eq. (35). Here, the half-filled and nonmagnetic case for the electron system in the metal substrate at finite temperatures is considered for simplicity.

The probability distributions for the dissociative scattering are calculated in the cases when the impinging molecule has an initial orientation $\theta = 10°$, $70°$, and $90°$ with respect to the surface normal, by changing the magnitude of the Coulomb interaction U. The numerical results are shown as functions of the released kinetic energy and the final translational energy in Figs. 7(a) and 7(b). The results of the probability distribution as functions of the released kinetic energy (Fig. 4) and the final translational energy (Fig. 6) are the cross sections of Fig. 7(a) cut by the planes for which the final translational energy and the released kinetic energy are constant, respectively. It is found from Eq. (29) that the energy of the metal electron system at finite temperatures is unchanged on the solid line in Fig. 7 ($A = 0$), increases on the low energy side of the solid line ($A < 0$), and decreases on the high energy side of the solid line ($A > 0$). It is shown in Fig. 7 that as the magnitude of the Coulomb interaction is increased, the dissociation probability increases on the high energy side of the solid line, i.e., the energy of the metal electron system in the initial state at finite temperatures decreases. It is also shown that an orientation dependence with a parallel orientation preference can be seen in the high energy region where the dissociation probability increases as the magnitude of the Coulomb interaction is increased.

The cross sections of Fig. 7(b) cut by planes for which the released kinetic energy is constant ($\varepsilon_{KIN} = 4.7$ eV and 7.0 eV) are shown in Fig. 8 (which is the probability distribution as a function of the translational energy in the case when the Coulomb interaction is taken into account). It is found from Figs. 6 and 8 that as the magnitude of the Coulomb interaction is increased, the probability for the dissociative scattering increases in the high energy region of the probability distribution, where the tail structure of the probability distri-
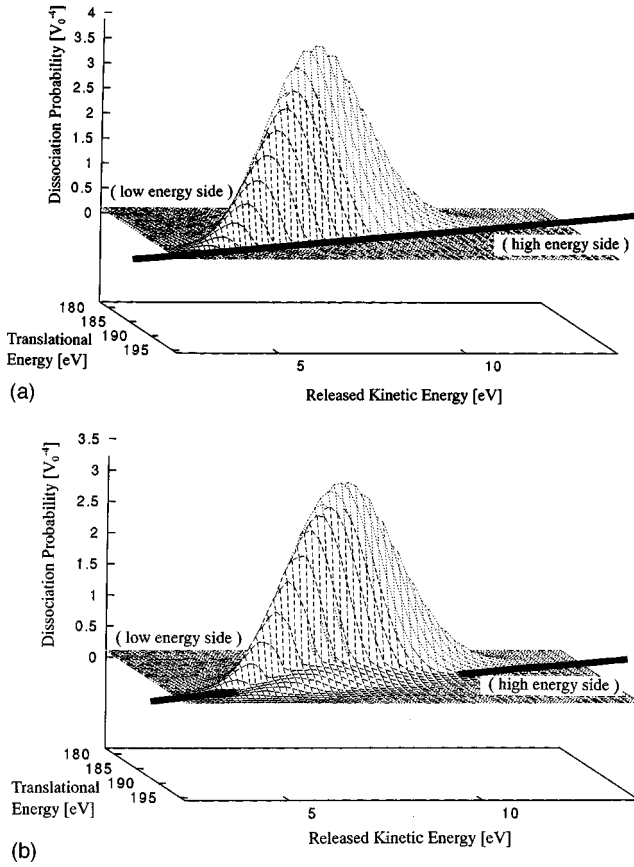
(a)

(b)

FIG. 7. Dissociation probability as a function of the released kinetic energy ε_{KIN} and the translational energy $\varepsilon_{c.m.,f}$ for molecular orientations $\theta = 10°$ and $90°$. The region of a near-perpendicular orientation preference is shown by the dotted lines, and the region of a parallel orientation preference is shown by the broken lines. In the calculation, the following parameter values are used: $\gamma = 0.7$ bohr^{-1}, the metal substrate temperature $T_S = 500$ K, the filled-band width $D = 4$ eV, and $\varepsilon_{c.m.,i} = 200$ eV for the impinging molecule.

FIG. 8. Dissociation probability as a function of the translational energy $\varepsilon_{c.m.,f}$ for molecular orientations $\theta = 10°$, $70°$, and $90°$, taking account of the Coulomb interaction in the metal substrate. We calculate the probability distributions in the cases that $\varepsilon_{KIN} = 4.7$ eV and 7.0 eV, and the parameter values $\gamma = 0.7$ bohr^{-1}, the metal substrate temperature $T_S = 500$ K, the filled-band width $D = 4$ eV, $U = 2$ eV, and $\varepsilon_{c.m.,i} = 200$ eV for the impinging molecule.

excitation of electron-hole pairs in the dissociative scattering to proceed, the electron-hole pairs must be present across the Fermi level in the initial state of the electron system at finite temperatures. Such electron-hole pairs are present naturally in the initial state of the interacting electron system ($U > 0$) at finite temperatures, but scarcely in the noninteracting electron system ($U = 0$). As a result, the probability distribution for the dissociative scattering in the interacting electron system increases on the high energy side of the solid line.[28]

Then, the enhancement of the parallel orientation preference at the high energy region of the probability distribution is considered. In the noninteracting electron system at finite temperatures, occupied states are mainly located below the Fermi level, from which electrons can transfer to the molecule. In the interacting electron system, on the other hand, electron-hole pairs are naturally present around the Fermi level and electrons with large wave number can exist, so electrons with large wave number can transfer to the mol-

bution shows up in both cases of $\varepsilon_{KIN} = 4.7$ eV and 7.0 eV. It is also found that at the main peak of the probability distributions for $\varepsilon_{KIN} = 4.7$ eV ($\varepsilon_{c.m.,f} = 183$ eV – 190 eV) and 7.0 eV ($\varepsilon_{c.m.,f} = 186$ eV – 192 eV), the orientation dependence of the probability distribution for the dissociative scattering in the interacting electron system turns out to be qualitatively the same as that in the noninteracting electron system. On the other hand, at the high energy tails ($\varepsilon_{c.m.,f} \geq 190$ eV when $\varepsilon_{KIN} = 7.0$ eV and $\varepsilon_{c.m.,f} \geq 192$ eV when $\varepsilon_{KIN} = 4.7$ eV, respectively), an orientation dependence with a parallel orientation preference can be seen. The cross sections of Fig. 7(b) cut by planes for which the final translational energy is constant ($\varepsilon_{c.m.,f} = 184.0$ eV, 188.5 eV, and 190.0 eV) are shown in Fig. 9 (which is the probability distribution as a function of the released kinetic energy in the case that the Coulomb interaction is taken into account). In Fig 9, we can see the same tendency as shown in Fig. 8.

The increase in the dissociation probability in the high energy region is explained as follows. In the high energy tail ($A > 0$), the energy of the metal electron system in the initial state at finite temperatures decreases due to deexcitation of electron-hole pairs in the dissociative scattering. For the de-
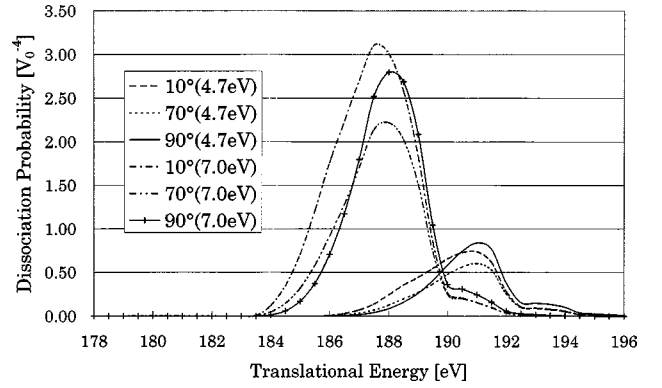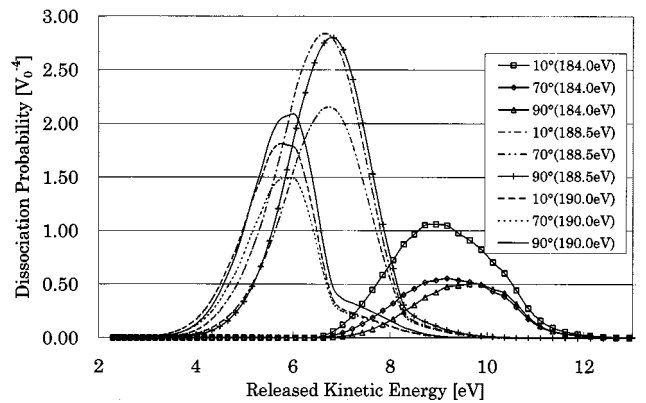

FIG. 9. Dissociation probability as a function of the released kinetic energy ε_{KIN} for molecular orientations, $\theta = 10°$, $70°$, and $90°$, taking account of the Coulomb interaction in the metal substrate. We calculate the probability distributions in the cases that $\varepsilon_{c.m.,f} = 184.0$ eV, 188.5 eV, and 190.0 eV, and the parameter values $\gamma = 0.7$ bohr^{-1}, the metal substrate temperature $T_S = 500$ K, the filled-band width $D = 4$ eV, $U = 2$ eV, and $\varepsilon_{c.m.,i} = 200$ eV for the impinging molecule.
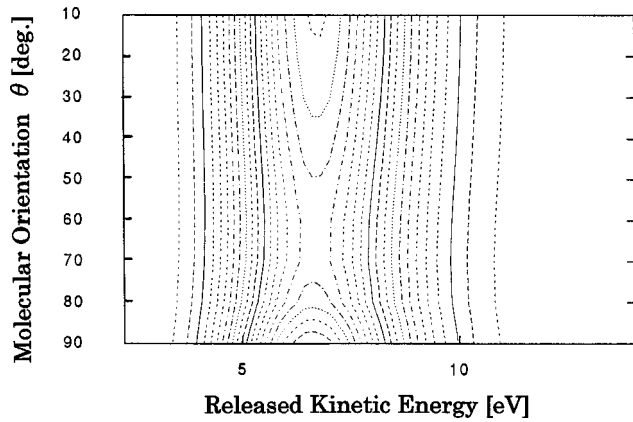
FIG. 10. Distribution of released kinetic energy as a function of the molecular orientation for dissociative scattering, summing up with respect to the final translational energy $\varepsilon_{c.m.,f}$. Contour spacing is $1.2 V_0^{-4}$, and the height of the probability peak in the case of the molecular orientation $\theta = 10°$ and the released kinetic energy $\varepsilon_{KIN} = 7$ eV is approximately $21.4 V_0^{-4}$. For the case of $\theta = 90°$ and $\varepsilon_{KIN} = 7$ eV the height is approximately $22.5 V_0^{-4}$. In the calculation, the following parameter values are used: $\gamma = 0.4$ bohr^{-1}, the metal substrate temperature $T_S = 500$ K, the filled-band width $D = 4$ eV, $U = 0$ eV, and $\varepsilon_{c.m.,i} = 1000$ eV for the impinging molecule.

ecule. In addition, from Eqs. (27), (32), and (33), even if the magnitude of the Coulomb interaction is increased, the wave number of electron states involved in the process remains practically unchanged in the single-site approximation although the number of electrons involved in the process increases.[20] So, in the main peak, qualitatively the same results are obtained for the orientation dependence of the probability distribution whether we consider the interacting electron system or the noninteracting electron system. At the high energy tail that appear as the magnitude of the Coulomb interaction increases, electrons with large wave number transfer to the molecule and the value of $k'r$ is large for any molecular interatomic distance r. Here the orientation dependence of the dissociation probability with a parallel orientation preference can be seen.

D. Comparison of the experimental and numerical results

The probability distribution as functions of the released kinetic energy and the molecular orientation with respect to the surface normal is experimentally reported by Harder *et al.*[13,16] In the experiment, hydrogen molecules with the high translational energy (500 eV–1000 eV) are scattered from metal substrate. The numerical result is shown as functions of the released kinetic energy and the molecular orientation with respect to the surface normal in Fig. 10. The

probability distribution is summed up with respect to the final translational energy $\varepsilon_{c.m.,f}$. The orientation dependence of the probability distribution in the interacting electron system is qualitatively the same as that in the noninteracting electron system, because the characteristic structures showing up as the magnitude of the Coulomb interaction increases cannot be seen in the probability distribution summed up with respect to $\varepsilon_{c.m.,f}$. It is found from Fig. 1 in Ref. 13 and Fig. 10 that the orientation dependence of the probability distribution of the numerical results are qualitatively the same as that of the experimental results for the dissociative scattering at small incident angles, in that the dissociation probability increases in the cases when the impinging molecule has an initial orientation of $\theta = 10°$ and $90°$.

IV. SUMMARY

The probability distributions for dissociative scattering are calculated as functions of the released kinetic energy and the final translational energy in cases when impinging molecules have various orientations. On the basis of the calculation results, it is found that the orientation dependence of these probability distributions appears as a consequence of the interference of electron waves transferring between the hydrogen molecule and the metal substrate. Furthermore, probability distributions are calculated taking account of the Coulomb interaction between electrons in the metal substrate. It is found that as the magnitude of the Coulomb interaction is increased, a parallel orientation preference is enhanced at the high energy region of the probability distribution. The probability distributions are summed with respect to the released kinetic energy ε_{KIN}. The obtained results for the probability distribution as a function of the final translational energy are qualitatively the same as the previous results for the case in which the molecular interatomic distance is fixed at its equilibrium distance.[20] It is also found that the orientation dependence of the probability distributions of numerical results is qualitatively the same as that of the experimental results reported by Harder *et al.*

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