

BULLETIN

OF THE

KOREAN CHEMICAL SOCIETY

ISSN 0253-2964
Volume 24, Number 6

BKCSDE 24(6)
June 20, 2003

Articles

A Wavepacket Study on Translational Energy Distributions of the Photo-stimulated Desorbed Xe from an Oxidized Si(001) Surface

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Received February 26, 2003*

We report a quantum wavepacket study on the characteristic bimodal translational energy distribution of photo-stimulated desorbed Xe from an oxidized silicon (001) surface observed by Watanabe and Matsumoto, Faraday Discuss. 117 (2000) 203. We have simulated the theoretical translational energy distributions based on wavepacket calculations with a sudden transition and averaging model to reproduce the experiment. We discuss the desorption mechanism and suggest a very strong position dependence of the deexcitation processes for Xe/oxidized Si(001).

Key Words : Quantum wavepacket, Photo-stimulated desorption, Oxidized silicon surface

Introduction

Photo-stimulated desorption (PSD) has attracted considerable attention for its characteristic phenomena, which are quite different from those observed in conventional thermal desorption processes.¹ Quantum dynamical models to describe the PSD processes have been investigated²⁻⁸ mainly based on the Menzel-Gomer-Redhead model^{9,10} or Antoniewicz model.¹¹ Theoretical efforts have been devoted to including the effects of electronic quenching or other dissipation processes. The quantum dynamics of the desorption processes are now understood qualitatively, based on these models. However, in most of the theoretical studies, quantum dynamics calculations used semiempirical model potentials of electronic excited and ground states and assumed parameterized decay rates from excited to ground states. Although several studies for obtaining *ab initio* potential energy surfaces (PESs) of the electronic excited states of adsorbate/solid surface systems have been done,¹²⁻¹⁵ such studies are many fewer than that of the dynamics calculations. Theoretical studies that combine *ab initio* PESs with quantum dynamics calculations are even more limited.^{16,17} It is essential to use PESs that are as reliable as possible for quantum dynamics calculations in order to clarify quantitatively the PSD mechanisms including deexcitation processes.

Recently, Watanabe and Matsumoto irradiated nanosecond laser pulses on the oxidized Si(001) surface covered with Xe and detected the desorbed Xe atoms.¹⁸ A characteristic bimodal shape was observed in their time-of-flight (TOF) spectrum. Both components show high translational energies and the values are much larger than those expected from the conventional thermal desorption viewpoint. Furthermore, since the faster component was not observed when the photon energy was less than 3.5 eV, electronic excited states seem to play important roles in the desorption of this component. The translational energy of this component is narrowly distributed in the range of 0.40-1.4 eV, its average value being 0.80 eV.

Although Watanabe and Matsumoto expected that charge transfer states from Xe to the substrate were such electronic excited states, it is not clear whether these states do exist. Recently we have obtained the potential energy curves (PECs) for Xe/oxidized Si(001) by *ab initio* calculations,¹⁹ and we found that Xe was strongly attracted to the surface in the electronic excited state. Classical trajectory calculations with the sudden transition and averaging (STA) model²⁰ using our PECs could well reproduce the observed average translational energy within a reasonable lifetime range. However, the reason for the quite narrow distribution is still ambiguous.

In this study, we discuss the mechanism of PSD of Xe from the oxidized Si(001) surface in regard to the reason for the narrow translational energy distribution. Using our PECs we performed wavepacket calculations with STA, or with

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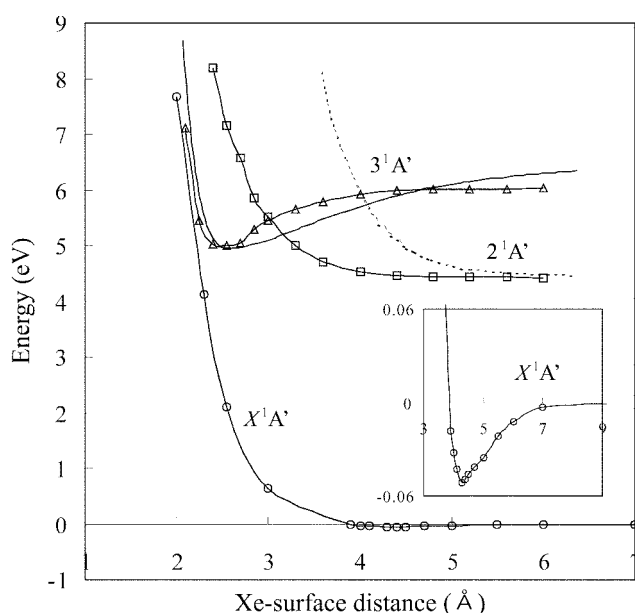


Figure 1. Potential energy curves calculated by *ab initio* methods [19] and modified PECs; a modified attractive PEC (solid line) and a modified repulsive PEC (dotted line). The inset is the enlargement of the ground state PES.

the jumping wavepacket model of Gadzuk²⁰ and its variant, a generalized jumping wavepacket model of Saalfrank.²¹ We focus only on the faster component, because the slower component is considered to be derived from anion intermediate states, Xe^- or clustering Xe_n^- .¹⁸

Methods

Potential energy curves. We used a cluster model to represent the oxidized Si(001) surface and calculated the PECs in the electronic ground and excited states by the fourth-order Møller-Plesset perturbation method with single, double, and quadruple substitutions (MP4(SDQ)) and the state-averaged complete active space self-consistent field (CASSCF) method, respectively. Several cluster models were studied, and we found that Xe is strongly attracted to the surface in the excited state for a model cluster that takes into account backbond oxidation. Figure 1 shows the PECs for the ground and excited states of the system, where the adiabatic $2^1A'$ and $3^1A'$ states cross and the non-adiabatic interaction between these states is considered to be very weak. Therefore, a diabatic picture is more suitable, by use of diabatic attractive and repulsive PECs in the electronic excited states. The observed average translational energy was reproduced effectively by classical trajectory calculations using the attractive PEC. Since excitation to the repulsive PEC does not seem to cause desorption because of the flat PEC at the Franck-Condon point, we did not examine the repulsive PEC. We discuss here the excitation to the attractive PEC and the repulsive PEC cases, taking a modification of the PECs into account.

Wavepacket calculations with the STA model. In order to obtain the expectation value and the distribution of

translational energy of desorbed Xe, we performed wavepacket calculations with the STA model.²⁰ In this model the wavepacket on the electronic ground state is excited initially and then propagates on the electronic excited state PEC. At a lifetime τ_n , a transition from the excited state to the ground state takes place suddenly. The wavepacket subsequently propagates on the ground state.

We use the system Hamiltonians

$$\hat{H}_{g,e} = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial x^2} + V_{g,e}(x), \quad (1)$$

where μ is the reduced mass, g and e denote the ground and excited states, $V(x)$ is the potential energy, x is the distance from the surface to the Xe.

The wavepacket after deexcitation is given by

$$\varphi(t; \tau_n) = \exp(-i\hat{H}_g(t - \tau_n)/\hbar) \exp(-i\hat{H}_e \tau_n/\hbar) \varphi(0), \quad (2)$$

and the expectation value for an operator \hat{A} at this time is given by

$$A(t; \tau_n) = \langle \varphi(t; \tau_n) | \hat{A} | \varphi(t; \tau_n) \rangle. \quad (3)$$

Considering the distribution of lifetimes and the exponential decay of the population in the excited state, we obtain the averaged expectation value from

$$\langle A(t) \rangle = \frac{\int_0^\infty d\tau_n e^{-\tau_n/\tau} \langle \varphi(t; \tau_n) | \hat{A} | \varphi(t; \tau_n) \rangle}{\int_0^\infty d\tau_n e^{-\tau_n/\tau}}, \quad (4)$$

where τ is an average lifetime and is assumed to be independent of the coordinate (*i.e.*, a constant). In practice, the integration in Eq. (4) is replaced with a summation. Equation (4) becomes

$$\langle A(t) \rangle = \frac{\sum_{n=1}^N e^{-n\Delta\tau_n/\tau} \langle \varphi(t; \tau_n) | \hat{A} | \varphi(t; \tau_n) \rangle}{\sum_{n=1}^N e^{-n\Delta\tau_n/\tau}}, \quad (5)$$

with $\tau_n = n\Delta\tau_n$ ($n = 1$ to N). The weighting factor $e^{-\tau_n/\tau}$ is determined analytically. However, the lifetime is likely to change as Xe approaches the surface. In order to include the effect of this coordinate-dependent lifetime, we make use of the generalized jumping wavepacket model suggested by Saalfrank *et al.*²¹ In this model, the weighting factor w_n is determined numerically by adding a negative imaginary potential to the excited state Hamiltonian,

$$\hat{H}_e = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial x^2} + V_e(x) - \frac{i}{2} \Gamma(x), \quad (6)$$

where $\Gamma(x)$ is the coordinate-dependent decay rate, which can be expressed as $1/\tau$ if it is constant. w_n is given by the product of survival probability at t_{m-1} and the jump probability at t_m . Equation (4) can be generalized if $e^{-\tau_n/\tau}$ is simply replaced with w_n .

The initial wavepacket in our calculations is regarded as the vibrational ground state wave function and is obtained from the harmonic oscillator approximation for the ground state PEC,

Table 1. Parameters used for wavepacket calculation

Timestep	Δt	1	fs
Life time grid	$\Delta \tau$	20	fs
Grid spacing	Δx	0.01	au
Starting point	x_0	0.01	au
Number of grid	N	24576	
Total propagation time	t_{\max}	5000	fs
Number of iteration (attractive)	n_{at}	26	
Number of iteration (repulsive)	n_{re}	35	
separation point	x_{des}	10	Å
wavepacket parameter	α	16.7318	au ⁻¹

$$\varphi(0) = \left(\frac{\kappa}{\pi}\right)^{1/4} \exp\left(-\frac{\kappa}{2}(x - x_e)\right), \quad (7)$$

where x_e means the equilibrium length. The wave function of the desorbed Xe, $\psi_{\text{des}}(x, t)$, is defined by introducing a separation point x_{des} and a cut-off function $f(x)$ that separate reactants from products. The $f(x)$ is expressed as

$$f(x) = 1 - \frac{1}{1 + \exp(\beta(x - x_{\text{des}}))}, \quad (8)$$

where β is a steepness parameter and $\psi_{\text{des}}(x, t)$ is given by

$$\psi_{\text{des}}(x, t) = f(x)\varphi(x, t). \quad (9)$$

Then the expectation value of the translational energy is obtained from

$$\langle E_{\text{trans}}(t) \rangle = \frac{\sum_{n=1}^N w_n \langle \psi_{\text{des}}(x, t; \tau_n) | -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial x^2} | \psi_{\text{des}}(x, t; \tau_n) \rangle}{\sum_{n=1}^N w_n \langle \psi_{\text{des}}(x, t; \tau_n) | \psi_{\text{des}}(x, t; \tau_n) \rangle} \quad (10)$$

We assumed that the separation point $x_{\text{des}} = 10$ Å and the desorption process was complete after 5 ps. The time propagation of the wavepacket was calculated using the Chebychev polynomial expansion with the FFT technique.^{22,23} The numerical parameters used are shown in Table 1.

If the relaxation rate depends on the coordinate, we assumed that it was proportional to the oscillator strength,

$$\Gamma(x, t) \propto \left| \int_0^\infty \Psi_f^*(x', t) \mu(x') \Psi_f(x', t) dx' \right|^2 (V_e(x) - V_e(x)), \quad (11)$$

where $\Psi_f(x)$ and $\Psi_i(x)$ are the final and initial wavefunctions respectively, and $\mu(x)$ is the electronic transition dipole moment obtained from *ab initio* calculations.

Results and Discussion

Wavepacket calculations using the diabatic attractive PEC. When the lifetime is 150 fs, the expectation value of the translational energy, calculated to be 0.76 eV, is nearly equal to the experimental value, 0.80 eV. In other PSD processes from oxide or semiconductor surfaces, the average lifetime is considered to be in the range of 10-100 fs.^{17,24,25} In comparison with this, the lifetime of 150 fs is considered to be reasonable. We then investigated the translational energy

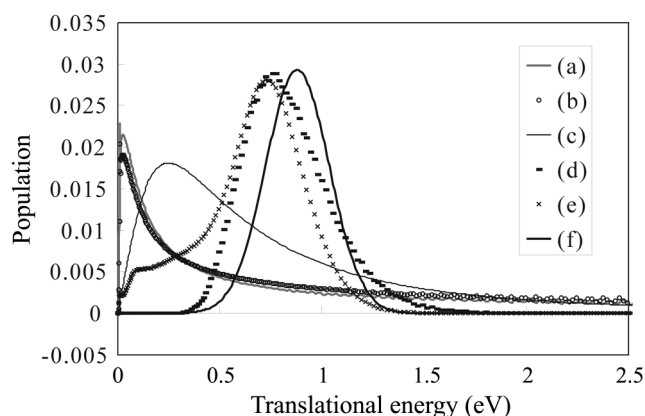


Figure 2. Translational energy distribution; (a) with a coordinate-independent decay rate on the attractive PEC ($\tau = 50$ fs), (b) coordinate-dependent decay rate on the attractive PEC, which is proportional to the oscillator strength, (c) by single trajectory on the original attractive PEC ($\tau_1 = 380$ fs), (d) by single trajectory on the modified attractive PEC ($\tau_1 = 240$ fs), (e) coordinate-independent decay rate on the modified repulsive PEC ($\tau_1 = 200$ fs) and (f) Ref. [18].

distribution (see Fig. 2). The translational energy observed in the experiment is narrowly distributed in the range of 0.4-1.4 eV (Fig. 2(f)). On the other hand, the translational energy distribution obtained in our wavepacket calculation (Fig. 2(a)) is spread widely, and its shape is obviously influenced by the exponential decay. That is, the low translational energy components, whose lifetimes are short, have large weights. This discrepancy between the experiment and the calculation shows that describing the relaxation process by the exponential decay may not be adequate. Therefore, we introduced the position dependency of the electronic deexcitation; the relaxation rate is proportional to the coordinate-dependent oscillator strength²⁰ between the ground and the diabatic attractive states. However, the translational energy distribution in Figure 2(b) did not show any significant changes.

The next attempt was to calculate the distribution from a single wavepacket trajectory with a fixed lifetime. This implies a very strong position dependence of electronic deexcitation; the electronic deexcitation occurs at a rather narrow region of the excited state PEC. Although the shape for $\tau = 380$ fs (Fig. 2(c)) is no longer an exponential decay, it is still far from a Gaussian; it is broadened and its peak is positioned at a lower translational energy. There are two reasons for the shape of the distribution. The first reason is the gradient around the Franck-Condon point. Since the left half of the wavepacket is more accelerated than the right half, this asymmetric shape is obtained. The second reason is the long time propagation, which causes broadening of the wavepacket. After the deexcitation, the head of this broadened wavepacket gains much more translational energy from the steeply repulsive wall of the ground state PEC. The translational energy is therefore distributed widely. That is, the wavepacket must be accelerated uniformly within such a short time that the wavepacket is not broadened. In order to fulfill this condition, we have modified the gradient of the excited state PEC at the Franck-Condon point (Fig. 1). This modification of our *ab initio* PEC may be due to the fact that

the CASSCF method is not sufficient to describe an ionic interaction, that is the origin of attractive interaction of the state. The result for $\tau = 240$ fs is shown in Fig. 2(d). Although the width of the translational energy distribution is slightly wider than that of the experiment, they are in good agreement. It is therefore adequate to assume that electronic quenching occurs within a narrow range.

Gortel and Wierzbicki suggested a squeezed wavepacket model²⁶ to avoid a very strong position dependence of electronic deexcitation, which is usually physically unjustified, for a system where the equilibrium positions of the excited and the ground state PECs nearly coincide. However, our situation is rather different from theirs. Here, we try to justify our assumption of the very strong position dependence of electronic deexcitation based on our *ab initio* electronic structure of Xe/Si(001). According to our calculations, each Si dangling bond has one electron in the electronic ground state (*i.e.*, open-shell singlet structure); in the electronic excited state (diabatic attractive state), the electron in the dangling bond where Xe is adsorbed is transferred to the other dangling bond. This unoccupied dangling bond is energetically lower than the occupied one and the deexcitation means that the electron in the occupied dangling bond returns to the unoccupied dangling bond. We found that the energy level of the unoccupied dangling bond shifts higher as Xe approaches the surface. Furthermore, the energy levels of the occupied and unoccupied dangling bonds are degenerate when the distance from the surface to the Xe is 3.2 Å, which corresponds well to the expectation value of the position of Xe, 3.28 Å, at $\tau = 240$ fs (Fig. 2). Based on a perturbation theory, it may be reasonable to expect a resonance transition between the two degenerate dangling bonds, *i.e.*, localized electronic deexcitation.

Wavepacket calculations using the diabatic repulsive PEC. We have also calculated the translational energy in excitation to the diabatic repulsive PEC. No desorption occurs unless this PEC is modified. In order to reproduce the experimental distribution we have to shift the excited PEC by 1.15 Å (Fig. 1). When the average lifetime is 200 fs, the expectation value of the translational energy is calculated to be 0.60 eV and the translational energy distribution is shown in Fig. 2(e). Although a small peak exists in the low translational energy region, a quite narrow distribution is obtained. Since all components whose lifetimes are longer than a critical lifetime have nearly equal translational energies, a sudden electronic quenching is not necessary in this case. The observed narrowly distributed translational energy can be reproduced by describing the deexcitation process within the usual exponential decay regime. However, in order to reproduce the experimental distribution, we have to modify our *ab initio* PECs significantly, which is not acceptable within our theoretical level. We may therefore conclude that this diabatic repulsive state is not relevant to the fast component of the distribution.

Conclusions

Photo-stimulated desorption of Xe from an oxidized

Si(001) surface has been simulated by quantum wavepacket calculations with the STA model. When the system is excited to the diabatic attractive PEC, it takes 150 fs as the average lifetime to obtain the translational energy observed in the experiment. This value is reasonable in comparison with those of metal oxides or semiconductor surfaces. However, the theoretical translational energy distribution shows an exponential decay and is quite different from the Gaussian distribution of the experiment. Nevertheless, we have effectively reproduced the experimental Gaussian distribution by consideration of a very strong position dependence of the electronic deexcitation and a modification of the gradient at the Franck-Condon point. This localized electronic deexcitation has been related to a resonance transition between the degenerate dangling bonds.

Acknowledgements. This research was supported by a Grant-in-aid for The 21st Century COE Program for Frontiers in Fundamental Chemistry and for Scientific Research (B) (#14340174) from the Ministry of Education, Culture, Sports, Science and Technology of Japan. The authors are grateful to Prof. Y. Matsumoto for fruitful discussions and thank the Computer Center of the Institute for Molecular Science for the use of computers.

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