

Theoretical Modeling of Steric Effect in Electron-Induced Desorption: CH₃Br/O/Ru(001)

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A theoretical model is presented to examine recently reported steric effects in electron–adsorbate interactions. The model is based on a short-lived anionic excited state formed by vertical photoelectron transition. An initial wave packet propagates on the excited-state potential and is quenched back to the ground state after a short residence time. The acquired momentum is the origin for desorption and dissociation. It is shown by quantum time-dependent modeling of the process that the orientation of the molecule has a profound effect on the kinematics of the photodesorption. The Br-up configuration is calculated to have a much larger desorption cross section. It is predicted that the adsorbed molecule tilt angle with respect to the surface normal is larger for the Br-up configuration.

I. Introduction

Steric effect in chemical dynamics is a well-studied subject.^{1,2} Recently, a steric effect in desorption induced by electronic transition (DIET) of a methyl bromide molecule, CH₃Br, on a partially oxidized Ru(001) surface was reported.³ The position of the Br atom pointing either toward the surface or to the gas phase was controlled electrostatically by the coverage of preadsorbed oxygen on a Ru(001) surface. Once a configuration of adsorbed CH₃Br was stabilized, desorption or dissociation was induced either with photons or by low-energy electrons. The orientation of the molecule was found to have a profound influence on the outcome of the reaction. The Br pointing up had a larger photoinduced desorption rate as compared to the Br pointing down. When electrons were used, this effect was reversed. The present paper is a theoretical investigation into the origins of this steric effect.

When a photon is absorbed by a metal covered by adsorbates, the prominent process converts the photon energy to production of electron–hole pairs. The secondary electrons from this process then attach to the adsorbed molecules creating a short-lived molecular ion. In most cases, the attached electron becomes quenched back to the metal within a time scale of less than ~10 fsec. A competing minority channel is dissociative electron attachment (DEA). Other experiments with sources of low-energy electrons show analogous dynamics induced by electron attachment.^{4,5} Similar effects are observed by slow electrons from above or induced by the tunneling current from an STM tip.^{6,7} Once a molecular ion is formed, it becomes attracted to the surface as a result of image forces. As a result, the molecule accelerates toward the metal surface, thus increasing the momentum along the molecule surface coordinate. Quenching of the attached electron gates the excited state nuclear dynamics. Finally, the continued evolution on the ground electronic surface determines the outcome of the photoinduced process. The

theoretical framework of desorption induced by electronic transition (DIET) is, therefore, common to all processes induced by electron attachment. The steric effects observed in the CH₃Br/O/Ru(001) system can, therefore, be attributed to either the process of electron attachment or the ensued nuclear dynamics.

To evaluate the relative importance of the reported steric effect of desorption and dissociation, the energy of the attaching electron has to be estimated. The photoinduced experiments were performed with photon energies of 5 and 6.4 eV. Taking into consideration the effective work function and the stabilization of the negative molecular ion due to its image charge within the metal, the energy of the attaching electron was estimated to be in the range of ~1 to 3 eV. The electron energy of the direct electron induced experiment was in the range of 10 eV; therefore, the difference in the electron energy between the two experiments is ~8 eV.

In the theory of electron attachment, the first step is attributed to an empty unoccupied orbital of the molecule. The first available electronic orbital is the lowest unoccupied molecular orbital (LUMO). Calculations for CH₃Br in the gas phase show that the energy of this orbital is 2.1 eV.⁸ The LUMO orbital has its nodal planes perpendicular to the molecular axis with almost equal terminal lobes on the Br and CH₃ sides. Higher energy electrons may attach to unoccupied molecular orbitals with different symmetry. The next unoccupied orbitals are centered on the methyl group. Measurements of total cross section for electron scattering from CH₃Br in the gas phase identify a small peak at ~2 eV attributed to the LUMO.⁸ In addition, a broad resonance at ~10 eV is observed for CH₃Br as well as for CH₃Cl and CH₃I.

Experimentally, the orientation of methyl bromide on an O/Ru(001) surface was controlled by varying the amount of adsorbed oxygen.³ The presence of the oxygen changes the surface charge distribution and, thus, the work function of the

overall system. The outcome of this change is that the orientation of the CH₃Br flips at the second layer.³ The CH₃Br adsorption geometry at low oxygen coverage (0.35 ML), is such that the bromine side is pointing upward, away from the surface, while at high oxygen coverage (0.65 ML), the bromine is pointing down toward the surface. The two adsorption configurations will be denoted as Br-up and Br-down configurations, respectively. In the photon-induced experiment, the cross section for Br-up desorption is three times larger than for Br-down.³ The cross sections for electron-induced desorption shows a slightly greater probability of desorption for Br-down configuration than for the Br-up (electrons from the vacuum side).

The model of the process is based on partitioning the total cross section to the product of the electron attachment and the MGR-DIET dynamics, for example, $\sigma \approx \sigma_{\text{cap}} P_{\text{quench}}$.⁹ The model of the electron attachment will not be considered explicitly. The present study focuses on the steric effects in the nuclear dynamics. The model follows the MGR scheme^{10,11} combined with the Gadzuk jumping wave packet approach.^{12,13} The probability of desorption is given as an average over all the possible residence times of the anionic state.

II. Model

The desorption dynamics of CH₃Br on the O/Ru(001) surface is simulated by a two-dimensional model including two diabatic potential energy surfaces (PES). This model is based on a flat surface approximation; hence, the interaction between the molecule and the surface is translationally invariant along the surface and rotationally invariant around the surface normal. The orientation of the axis of the molecule is chosen perpendicular to the surface. Furthermore, all degrees of freedom involving the internal motion of CH₃ are frozen. The two degrees of freedom that are selected for explicit description are the intramolecular distance between the bromine and the methyl (r) and the molecular center of mass distance relative to the surface (Z). The total mass and the reduced mass are denoted here by M and μ . The process is described by two electronic states: the ground state, V_g , and a single anionic excited state, V_e . The ground state describes the interaction of the neutral adsorbate with the O/Ru(001) surface. The anionic state represents the anionic adsorbate interacting with the substrate. The two potential energy surfaces are based on semiempirical model potentials.

A. The Electronic Ground-State Potential. The ground-state potential represents a strong CH₃–Br bond and a much weaker CH₃Br–surface bond.

$$V_g(r, Z) = V_{\text{Ru-CH}_3\text{Br}}(r, Z) + V_{\text{CH}_3\text{Br}}(r) \quad (1)$$

The same functional form is used to describe V_g for the two different configurations, reflecting the fact that the binding energies for the two adsorption geometries on the O/Ru(001) surface are known experimentally to be almost identical. Furthermore, the binding energies of both the methyl fragment and the bromine fragments on various surfaces are nearly identical.^{14–16} The potentials are constructed such that the interaction between the surface and the molecule is dominated by the binding of the fragment closest to the surface. A modified Morse potential form is used. The locations of the bromine atom and the methyl fragment are related to the two degrees of freedom by the following relations $z_{\text{Br}} = Z - Cm_{\text{CH}_3}r/M$ and $z_{\text{CH}_3} = Z + Cm_{\text{Br}}r/M$, respectively. The function, C , depends on the molecular orientation, and it takes the value $C = 1$ for Br-down and $C = -1$ for Br-up. For the Br-up configuration

(e.g. $z_{\text{Br}} > z_{\text{CH}_3}$), the surface–molecule interaction is given by

$$V_{\text{Ru-CH}_3\text{Br}}(r, Z) = D_R [e^{-2\alpha_R(z_{\text{CH}_3} - Z_{\text{up}}^e)} - 2e^{-\alpha_R(z_{\text{CH}_3} - Z_{\text{up}}^e)}] \quad (2)$$

whereas for the Br-down configuration ($z_{\text{Br}} < z_{\text{CH}_3}$), the potential becomes

$$V_{\text{Ru-CH}_3\text{Br}}(r, Z) = D_R [e^{-2\alpha_R(z_{\text{Br}} - Z_{\text{down}}^e)} - 2e^{-\alpha_R(z_{\text{Br}} - Z_{\text{down}}^e)}] \quad (3)$$

The equilibrium distance between the surface and the two fragments differs, since the van der Waals radii of the bromine is greater than the one of the methyl fragment. The explicit expressions become

$$\begin{aligned} Z_{\text{down}}^e &= Z_e \\ Z_{\text{up}}^e &= Z_e + \frac{(m_{\text{Br}} - m_{\text{CH}_3})r_e}{M} - Z_0 \end{aligned} \quad (4)$$

The same set of parameters of $\{D_R, \alpha_R, Z_e\}$ is used for the potential energy surfaces associated with both adsorption configurations. The parameter Z_0 has been chosen such that the binding energy between the surface and the molecule reproduces the experimental value of 0.34 eV for the two adsorption configurations.

The intramolecular potential is also represented by a Morse potential,

$$V_M(r) = D_M [e^{-2\alpha_M(r-r_e)} - 2e^{-\alpha_M(r-r_e)}] \quad (5)$$

The parameters used for the equilibrium distance and the dissociation energy of methyl bromide are given in ref 17. The parameter, α_M , has been adjusted to fit the vibrational frequency of methyl bromide of 75.8 meV.¹⁸

B. The Anionic State Potential. The electronic excited potential energy surface describes the anionic adsorbate interacting with the O/Ru(001) surface. The following functional form is used.

$$V_e(r, Z) = V_{\text{Ru-CH}_3\text{Br}}(r, Z) + V_{\text{CH}_3\text{Br}^-}(r) - \text{EA} + \phi + V_{\text{im}}(Z) \quad (6)$$

The electron affinity of the methyl bromide is denoted EA, and the work function of the Ru(001) surface is denoted by ϕ . The work function of a bare surface is used in the present study. This value was estimated from DFT calculation.¹⁹ It should be noted that no explicit description of the oxygen layer is used in the model. As the oxygen is adsorbed onto the surface, the work function changes, leading to the anionic excited potential energy surface's being shifted relative to the ground-state surface.

For the intramolecular potential energy describing the charged molecule, an exponential repulsive potential is used.

$$V_{\text{CH}_3\text{Br}^-}(r) = B_{\text{ion}} e^{-\beta_{\text{ion}}(r-r_e)} \quad (7)$$

This functional form has been used for modeling of dissociative electron attachment of methyl bromide studied in the gas phase.^{20,21} The parameters, B_{ion} and β_{ion} , can be fitted to reproduce the excitation energy observed in the experiment.

The surface molecule interaction for the anionic state is described by a sum of a covalent binding chosen to be the same as for the ground state, together with a Coulomb interaction. Assuming the charge is located mainly on the bromine atom

TABLE 1: Parameters for the Potential Energy Surfaces

$D_M = 3.078$ eV	$\alpha_M = 1.703$ Å ⁻¹	$r_e = 1.933$ Å
$B_{ion} = 2.25$ eV	$\beta_{ion} = 5$ Å ⁻¹	EA = 3.37 eV
$D_R = 0.35$ eV	$\alpha_R = 1.8$ Å ⁻¹	$Z_e = 2.3$ Å
$Z_0 = 0.5$ Å	$Z_{im} = 0.5$ Å	$\phi = 5.27$ eV

(located at the center of mass), the image potential contribution to the excited-state potential energy is

$$V_{im}(Z) = -\frac{1}{4(Z - Z_{im})} \quad (8)$$

The parameters used to describe the potential energy surfaces for the ground and anionic electronic state are summarized in Table 1.

III. Dynamics

A. The Jumping Wave Packet Approach. The dynamics of the desorption process of methyl bromide from the O/Ru(001) surface is modeled by the “jumping wave packet method”, first suggested by Gadzuk.^{12,13} The initial wave function, $\Psi(Z, r)$, is chosen as the lowest eigenstate of the two-dimensional electronic ground-state PES. This eigenstate represents a bound methyl bromide molecule. In the next step, a Franck–Condon excitation occurs at time $t = 0$. The initial wave packet is excited vertically to the anionic state. During the electronic transition, the nuclear degrees of freedom are unchanged. It is important to stress that the electron attachment process is not treated explicitly in this “jumping wave packet approach”. On the excited state, the wave packet evolves according to the Hamiltonian of the anionic state. After a residence time, τ_R , the evolved wave packet is quenched back to the ground state by a vertical Franck–Condon transition. Finally, the wave packet propagates on the ground-state surface, where it can desorb as a molecule, dissociate, or remain trapped/bound on the O/Ru(001) surface. This sequence constitutes one “quantum trajectory”. At this time, the Hamiltonians corresponding to the ground and excited states are uncoupled. The wave function at the final time $t_f > \tau_R$ is written explicitly (using atomic units) as

$$\Psi(Z, r, t_f; \tau_R) = e^{-iH_g(t_f - \tau_R)} e^{-iH_e \tau_R} \Psi_0(Z, r) \quad (9)$$

where the Hamiltonian operators of the system are given by

$$H_i(r, Z) = -\frac{1}{2M} \frac{\partial^2}{\partial Z^2} - \frac{1}{2\mu} \frac{\partial^2}{\partial r^2} + V_i(r, Z) \quad i = \{e, g\} \quad (10)$$

The expectation values $A(t_f; \tau_R)$ of an operator, $\hat{A}$, of a single quantum trajectory becomes

$$A(t_f; \tau_R) = \langle \Psi(t_f; \tau_R) | \hat{A} | \Psi(t_f; \tau_R) \rangle \quad (11)$$

The mean quenching rate, $\Gamma = \tau^{-1}$, is the inverse of the mean lifetime of the anionic state, τ . The expectation values are computed by averaging over a large number of quantum trajectories weighted according to the residence times and the mean lifetime, τ .

$$\langle A(t_f; \tau) \rangle = \frac{\int_0^\infty A(t_f; \tau_R) \exp\left(-\frac{\tau_R}{\tau}\right) d\tau_R}{\int_0^\infty \exp\left(-\frac{\tau_R}{\tau}\right) d\tau_R} \quad (12)$$

An equally spaced grid of N_τ residence times in an interval $[\tau_{R,i}, \tau_{R,f}]$ is used for sampling. The time period of each quantum

TABLE 2: Computational Parameters^a

time step on the ground-state surface	δt_1	5 fs
time step on the anionic surface	δt_2	1 fs
propagation time	t_f	2 ns (5 ns)
no. of Chebychev polynomial	noch	100/120 ^b
Z-grid start	Z_{min}	4a ₀ (1a ₀)
Z-grid spacing	ΔZ	0.02a ₀ (0.04a ₀)
no. of Z-grid points	N_Z	2048 (1024)
r-grid start	r_{min}	1a ₀
r-grid spacing	Δr	0.025a ₀ (0.05a ₀)
no. of r-grid points	N_r	512 (1024)
desorption dividing flux line	Z_{des}	15a ₀
dissociation dividing flux line	r_{dis}	15a ₀
no. of quantum trajectories	N_τ	32
residence time start	$\tau_{R, min}$	0.5 fs
residence time spacing	$\Delta \tau_R$	0.5 fs

^a If two values are given, the first is for the Br-up configuration, whereas the second is for the Br-down configuration. ^b For the anionic and ground state propagation, respectively.

trajectory is t_f . It should be noted that the exponential weighting in the jumping wave packet approach is equivalent to a coordinate-independent quenching in the open-system density matrix approach.

The probability of the molecule’s escaping to the gas phase is obtained via a flux-resolved analysis carried out at an asymptotic value of $Z = Z_{des}$. The probability for desorption becomes the total accumulated desorbing flux.

$$P_{des}(t_f; \tau_R) = \sum_{i=1}^{N_t} J_{des}(t_i; \tau_R) \quad (13)$$

The flux current, J , is

$$J_{des}(t_i; \tau_R) = \frac{\delta t_2}{\mu} \text{Im} \left[\int dr \Psi^*(Z_{des}, r, t_i; \tau_R) \frac{\partial \Psi(Z, r, t_i; \tau_R)}{\partial Z} \Big|_{Z=Z_{des}} \right] \quad (14)$$

where the derivative is evaluated by a Fourier transform. δt_2 is the time step in the time propagation of the wave packet after the quenching process. The yield of desorption includes both molecules and the molecular fragments after dissociation.

B. Computational Details. The wave function is propagated on a two-dimensional (r, Z)-grid using the Chebychev propagation method.²² To prevent transmission and reflection of the wave function at large Z (and r), a complex exponential absorbing potential is used at the boundaries.^{23,24,25} The magnitude of the various parameters are summarized in Table 2. The dynamics corresponding to the two configurations is quite different; therefore, different grid settings are used for the two adsorption geometries. The simulation time to reach the desorption line for Br-down is larger than for the Br-up; therefore, longer propagation time is required for Br-down configuration.

IV. Results and Discussion

A. Initial State. The initial state of the process represents a methyl bromide chemisorbed on the O/Ru(001) surface. The lowest eigenstate of the two-dimensional ground-state potential is chosen to describe the initial state. This state is computed by using imaginary time propagation.²⁶ The energy of the lowest eigenstate is -3.38 eV for both the Br-up and Br-down configurations. The binding energy between the molecule and the surface was calculated to be -0.34 eV. The wave function of the lowest eigenstate serves as the initial wave packet for the “jumping wave packet approach” and is shown for the two configurations in Figure 1.

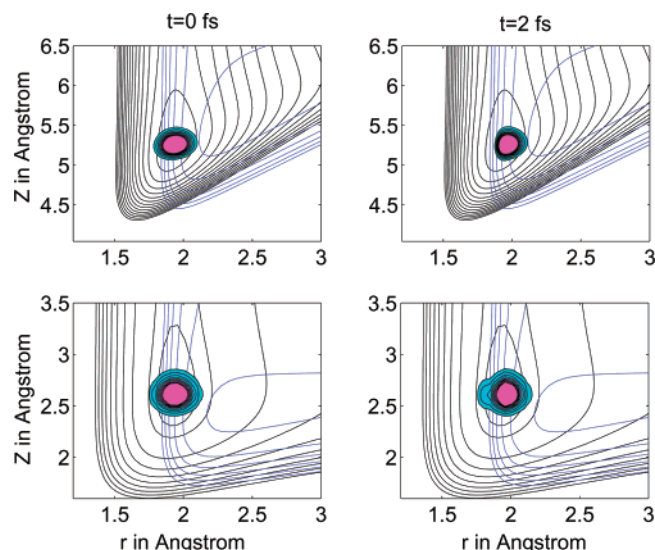


Figure 1. The upper panels show the dynamics of Br-up configuration, whereas the lower panels demonstrate the dynamics of the Br-down configuration. In the first column, the initial wave packet for both configurations is shown ($t = 0$ fs). The second column shows the wave packet at a residence time, $\tau_R = 2$ fs. The potential energy surfaces of the ground and the anionic states are displayed by black and blue contours, respectively. For the ground state, the contours are given for $\{-3.5, -3.25, -3, -2, -1, 0, 1, 2, 3, 4, 5\}$ eV and $\{0, 1, 2, 3, 4, 5\}$ eV for the anionic state.

B. Dynamics on the Anionic State. The initial wave packet is excited to the anionic electronic state through a Franck–Condon transition. The excitation energy becomes

$$E_{\text{ex}} = \langle \Psi_0 | \mathbf{H}_e | \Psi_0 \rangle - \langle \Psi_0 | \mathbf{H}_g | \Psi_0 \rangle \quad (15)$$

For the Br-up configuration, the excitation energy is calculated to be 6.34 eV, whereas for the Br-down configuration, it is 5.61 eV. The excitation energy differs because the stabilization of the anion upon excitation depends on the adsorption geometry. Upon excitation, the molecule finds itself on the strongly repulsive part of the excited potential energy surface. The initial movement of the wave packet on the anionic surface can be understood by analyzing the gradient of the potential energy. The gradient at the Franck–Condon point of the excited potential energy surface with respect to the intramolecular degree of freedom, dV_e/dr , is negative for both adsorption configurations. This implies that the wave packet moves to larger r , for example, the intramolecular bond length between the bromide and the methyl fragment increases. The gradient of the potential with respect to the molecular motion, dV_e/dZ , is positive for Br-down configuration and negative for the Br-up configuration. Since the center of mass is located almost on the bromine atom, the bromine moves close to the surface for the Br-down configuration, whereas in the Br-up configuration, the bromine moves farther away from the surface. The magnitude of the gradient with respect to center of mass motion is much smaller than the one corresponding to the intramolecular degree of freedom. The difference is about a factor of 5; therefore, the intramolecular motion dominates the dynamics of the wave packet immediately after the electronic excitation. Hence, energy is transferred into the intramolecular vibrational mode.

C. Desorption. After a specified residence time on the excited state, the wave packet is quenched back to the ground state. As the wave packet returns to the ground state, the two configurations show a very different dynamical behavior. Figures 1, 2,

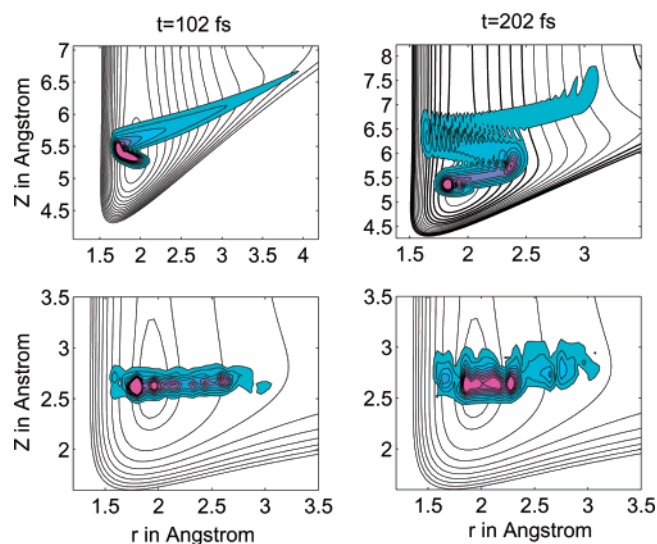


Figure 2. The left column shows the wave packets for the two configurations at time $t = 102$ fs, in the right column at $t = 202$ fs. Top panels correspond to Br-up, bottom panels to Br-down. Further details are given in Figure 1.

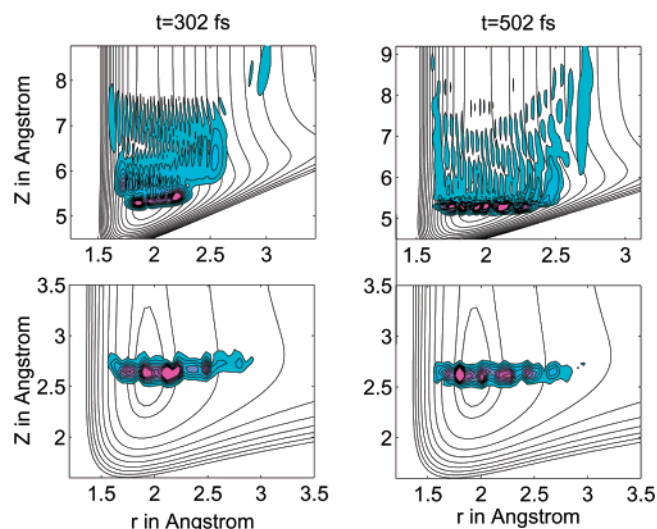


Figure 3. Same as Figure 1, left column for $t = 302$ fs and right column for $t = 502$ fs.

and 3 demonstrate the dynamics for the two configurations for a time sequence with the residence time of 2 fs. For the Br-up configuration, the methyl fragment bounces back and forth between the bromine atom and the surface since the movement of the bromide is very slow because of its large mass relative to that of the methyl fragment. This motion of the methyl fragment has been termed the chattering effect. It was also observed for CH_3Br on a $\text{LiF}(001)$ surface.^{27–29} For the Br-down configuration, the intramolecular distance increases as a function of the residence time and will eventually scatter back if the molecules do not gain enough energy to dissociate.

Analysis of the wave packet dynamics can indicate the adsorbate dissociation probability. The flux of desorbing molecules and fragments (methyl and bromide) has been computed by eq 3.1 as a function of the residence time τ_R . The flux dividing line does not distinguish between molecules and dissociated fragments. To differentiate the two processes, a state-resolved flux calculation is required in which the fluxes for all the vibrational states are computed. The accumulated flux of desorbing molecules for the two configurations is shown in

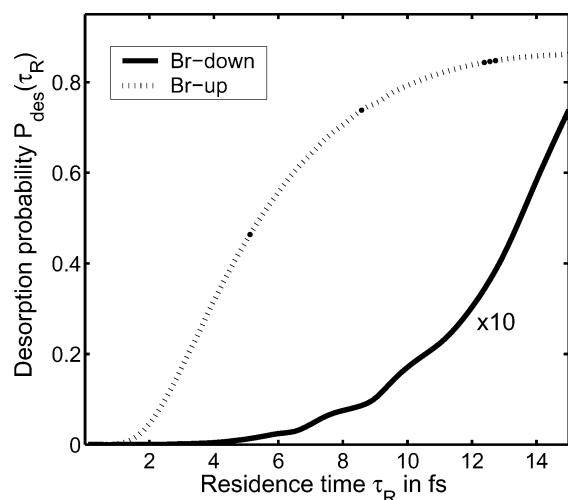


Figure 4. The probability for desorption, P_{des} , as a function of the residence time, τ_R , of the anionic state. The dividing line for the flux is at $Z = 15a_0$. The probability for desorption of Br-down has been scaled by a factor of 10.

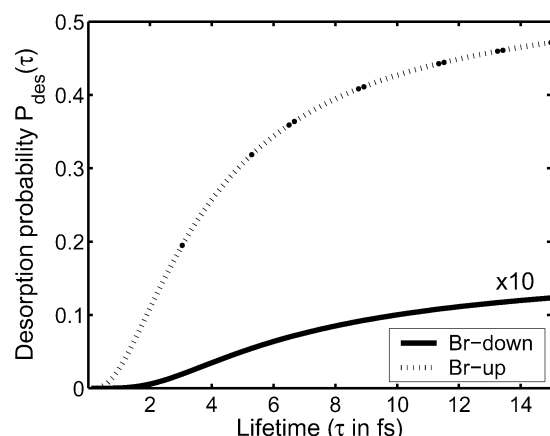


Figure 5. The weighted probability of desorption as a function of the mean lifetime, τ , of the anionic state. The probability for desorption of Br-down has been scaled by a factor of 10.

Figure 4. The Br-up configuration shows a much faster increase of the desorption probability when the residence time is increased.

The yield of the desorbing molecules as a function of the mean lifetime on the anionic state can be found by averaging over all the different residence times by using eq 3.1. The probability of desorption as a function of the mean lifetime on the anionic state is shown in Figure 5.

The higher yield observed for the Br-up configuration is due to the larger momentum gain in both degrees of freedom on the anionic state. In the Br-down configuration, momentum is primarily gained in the intramolecular degree of freedom. When the wave packet is quenched, it finds itself almost in the same Z position, as compared to its location prior to the excitation. Thus, it did not gain the necessary momentum to desorb. This observation, together with no chattering effect, explains why the dissociation yield for Br-down is greater than for desorption yield. The probability of dissociation was computed from the accumulating flux at $r = 15a_0$. The probabilities of dissociation are given as a function of the mean lifetime in Figure 6. The dissociated molecule leaves behind the fragment closest to the surface attached to it. For the Br-down configuration, this ratio is decreased to 2:1. The dissociation is a minority channel relative to desorption for Br-up. In the Br-up configuration, a typical ratio of 1:17 is calculated for a mean residence time of

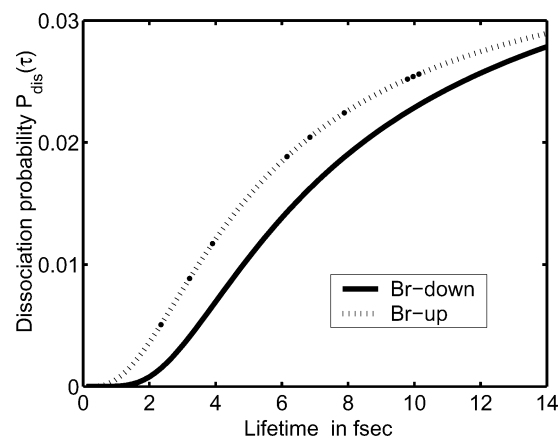


Figure 6. The probability for dissociation as a function of the mean lifetime of the anionic state. The dividing line for the flux is at $r = 15a_0$.

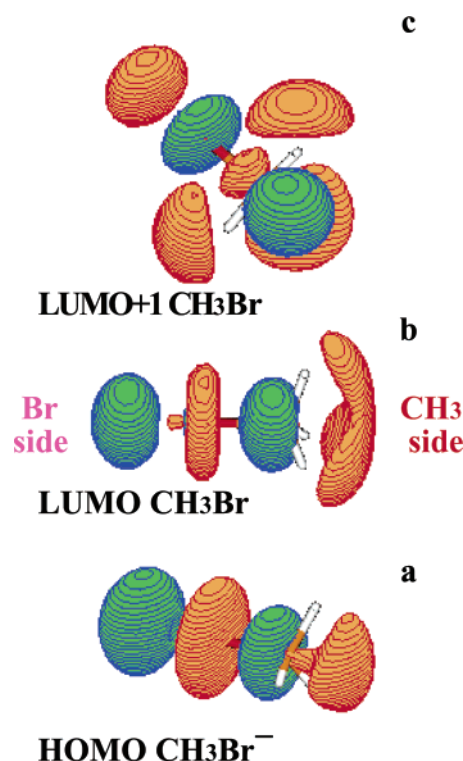


Figure 7. (a) The highest occupied molecular orbital, HOMO, of the molecular ion CH_3Br^- . (b) The lowest unoccupied molecular orbital, LUMO, of CH_3Br and (c) the next unoccupied molecular orbital, LUMO + 1, of CH_3Br . Calculation done at the MP2(full)/cc-pVDZ level. The two next unoccupied molecular orbitals are almost degenerate with LUMO + 1 and are also located on the methyl fragment.

10 fs. The probability of dissociation for the two adsorption configurations is almost the same.

D. Comparison with Experiment: Photon- vs Electron-Induced Desorption. Electron attachment is the governing factor in the dynamics of photon- or electron-induced desorption of adsorbates on surfaces. In the case of the $\text{CH}_3\text{Br}/\text{O}/\text{Ru}(001)$ system, rupture of the C–Br bond is an additional channel. For reactions induced by photoelectrons, the energy range is such that the electron attachment is through the LUMO orbital. In CH_3Br , the LUMO orbital has its nodal planes perpendicular to the molecular axis with almost equal terminal lobes on the Br and CH_3 sides.⁸ As a result, both sides of the molecule seem equally favorable for this attachment (cf. Figure 7). If the molecule adsorbs perpendicular to the surface, then no steric effect is expected for electron attachment for the dominant $k =$

0 electron momentum direction. In the presented model calculations, a steric effect was found in the nuclear dynamics of the MGR process, reminiscent of the heavy–light–heavy gas-phase reaction dynamics.^{1,2,30} The calculated steric factor due to the kinematic effect is 40:1 for an excited state means a lifetime of 10 fs. The experimental steric effect, however, is only 3:1. A possible explanation would be that the mean lifetime of the Br-down is significantly longer than that of the reversed orientation (a ratio of $\sim 10:1$ may lead to the experimental value). The quenching rate which determines the mean lifetime should be sensitive to the shape of the HOMO orbital of the CH_3Br^- . This orbital also has equal lobes at each side, therefore, excluding a significant steric effect in the quenching event (cf. Figure 7).

A major assumption in the model is that the molecules are oriented perpendicular to the surface. If the molecules are tilted, the electron attachment probability will significantly diminish, since the $k = 0$ plane wave of the ejected photo electrons will not match the periodic modulations of the LUMO orbital in this adsorption geometry. If the Br-up configuration is more tilted than the Br-down, then the calculated steric effect will shift toward a smaller ratio, as observed experimentally. Differential work–function measurements suggested, indeed, that the Br-up configuration may be somewhat more tilted.³

Electrons with 10-eV kinetic energy, as employed experimentally, are attached to higher lying unoccupied molecular orbitals of CH_3Br . These may have symmetries that are different from the LUMO. The next series of three unoccupied molecular orbitals were calculated, and they are located primarily on the methyl group, suggesting that the electron attachment event proceeds via the methyl side (see Figure 7). It is, therefore, plausible that for the 10-eV electrons, a larger attachment cross section will be found for molecules with the Br pointing down. Experimentally, the ratio of desorption rates of the Br-up to Br-down in this case is 1:1.4. To compensate the nuclear steric effect, the electron attachment cross section should be biased toward the methyl group by a factor of ~ 10 . This again may be explained by the asymmetric tilt angle of the two adsorption configurations and its influence on the quenching.

V. Conclusion

The origin of the steric effect in CH_3Br desorption on an oxygen covered Ru(001) surface were studied. Experimentally, the study was based on the ability to flip the adsorption geometry following coadsorbed oxygen density changes on Ru(001). Irradiation by 6.4-eV photons leads to desorption or dissociation via a substrate-mediated electron attachment mechanism. The theoretical modeling was aimed at the examination of the steric effect in either electron attachment, electron quenching, or nuclear dynamics. The molecular orbitals responsible for these processes do not show a predominant favorable geometry. Only tilting the molecule may reduce the electron attachment. More detailed calculations which include explicitly the surface and neighboring molecules may change these conclusions.

The subsequent nuclear dynamics is significantly biased toward the Br-up configuration. The 2-D quantum dynamical model shows an enhancement that is much larger than the experimental observation. Additional degrees of freedom, such as the tilt angle and the umbrella motion, may play a role. Simulations of the photodissociation in the gas phase of CH_3I show that the umbrella motion can remove only a minor fraction

of the available energy.^{31–33} The tilt motion, however, can be more important if the electron attachment of the molecule will move toward a perpendicular orientation and, thus, will shorten the excited-state mean lifetime. To explore these effects, a much more elaborate electronic structure and 4-D molecular dynamical calculations are required.

Direct excitation by a free electron from the vacuum side at an energy of 10 eV shows a reverse steric effect. In this case, the electron attachment mechanism can have a large bias toward the methyl side. This can balance the steric effect due to the nuclear dynamics in accordance with the experiment.

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