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CH_4 dissociation on Ni (111): A quantum dynamics study of lattice thermal motion

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ABSTRACT:

Lattice thermal motion is of great importance because it has a significant effect on molecule activation on metal surfaces. Here, we present an in-depth quantum dynamics study of lattice thermal motion for methane dissociation on some static distorted Ni(111) surfaces based on an accurate, fourteen-dimensional potential energy surface fitted to ~10^5 *ab initio* energy points. Our study reproduces the tendency that the sticking probability of ground state methane increases (decreases) as the lattice atom moves upward (downward), and thus represents the first validation of the applicability of the energy-shifting scheme to polyatomic molecular gas-surface reactions. Furthermore, we improve on the linear model proposed by Jackson's group and introduce a new model that is applicable to a broad range of surface temperatures.

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1. Introduction

The dissociative chemisorption of methane (CH_4) on transition-metal surfaces is a rate-limiting step in the catalytic steam reforming of natural gas. A large number of initial state-resolved scattering experiments have revealed mode- and bond-selectivity of CH_4 on Ni surfaces[1-7]. Surface temperature dependent experiments also unambiguously showed that lattice thermal motion has an important effect on methane activation[8] and results in a distinct temperature dependence upon different surfaces[9]. Accounting for such effects from first principles requires explicit treatment of degrees of freedom (DOFs) of all the substrate atoms in dynamics calculations. Once an approach for determining the interatomic forces of the substrate is classically prescribed, molecular dynamics (MD) simulations can be carried out for studying such effects. Shen *et al*[10,11] succeeded in reproducing bond-selectivity of methane and its deuterated isotopologues on Ni(111)and Pt(111) for experimental surface temperatures by means of an alternative approach combining quasi-classical MD and reactive force fields, including all the DOFs of the substrate. Nattino *et al*[12,13] studied CHD_3 dissociation on Ni(111) and Pt(111) at experimental surface temperatures by applying the *Ab Initio* Molecular Dynamics(AIMD) approach in which the interatomic forces are calculated on-the-fly from electronic structure calculations. The more convincing dynamics results, e.g., the pronounced tunneling effect on the C-H (D) bond activation in the low incident energy region, are preferable to obtain from quantum mechanical calculations. Substantial progress has been made on quantum dynamics studies of the dissociation behavior of CH_4 on a static surface[14-24]. Various approximations, such as surface oscillator model[16,17], surface mass model[17,18] and statistical model[19], have been introduced to take account of lattice thermal motion. Recently, Nave *et al* have extensively studied the surface temperature effects using the lattice-sudden model[20-22] applying a variety of sudden treatments. Density functional theory (DFT) calculations for transition state (TS) suggest that the targeted top metal atom over which CH_4 dissociates would be shifted upward to reduce the activation barrier[23]. Adding the DOF Q (lattice displacement in Z direction), lattice thermal motion was thus approximately modeled by allowing this targeted top metal atom over which the reaction occurs to move normal to the surface. The puckering[20] and recoiling[21] effects, i.e., so-called 'electronic coupling' and 'mechanical coupling' in the lattice-sudden model, can be roughly described with a linear model βQ and αQ for the variation of barrier height, where parameters β and α are phonon coupling parameters[24]. Using this model, the effect on the probability of CH_4 dissociation on the surface for different surface temperatures can be obtained from a post-treatment through an "energy-shifting" scheme[25]. These sudden quantum treatments have also lead to some successes in examining the dissociative chemisorption of hydrogen and water molecules on metal surfaces[26-29]. However, the applicability of the energy-shifting scheme used in the model to dissociative chemisorption of polyatomic molecules has never been validated, mainly due to the lack of the realistic and high-dimensional potential energy surface (PES) and accurate quantum models for the dynamics of polyatomic chemical reactions. Furthermore, recent studies have also revealed that the linear energy-shifting approximation in the model considerably underestimates the dissociation probability at high surface temperatures[29,30].

In this work, we report the results of a quantum dynamics study of lattice thermal motion using an eight-dimensional (8D) quantum model based on an accurate, high-dimensional potential energy surface fit to DFT total energy data. Our PES is a fourteen-dimensional (14D) global PES which fixes the CH_4 center of mass on the coordinate of the targeted top Ni atom but includes the DOF Q of Ni atom. Since it has 15 DOF of CH_4 interacting on a flat Ni(111) surface, our 14D PES means that it only ignores the effect of surface impact sites but importantly adds one more DOF of the targeted lattice vibration motion in Z direction. Through simulations of the sticking probability S_0 of the ground state (GS) CH_4 on the fixed top site of the static distorted Ni(111) surfaces with seven fixed Q values, we have validated the applicability of the energy-shifting scheme to polyatomic molecules interacting on metal surfaces. Moreover, we have demonstrated the validity of the linear model for lattice thermal motion proposed by Jackson's group in low to moderate surface temperatures and propose a new improved model applicable all the way from low surface temperatures to high surface temperatures.

2. Computational Method

In the description of methane-surface interaction, we first performed DFT calculations for CH_4/Ni(111) which were then used to fit a neural network (NN) potential energy surface. The Ni(111) surface has been modeled by a four layer slab and a (2x2) unit cell with a vacuum space between consecutive slabs corresponding to six metal layers. A Monkhorst-Pack grid of 3x3x1 *k*-points was used. The current set up is reasonable for needing huge of *ab* initio energy points. The fitting process using the NN method is very similar to that successfully implemented recently by some of us for gas-gas reaction[31] and gas-surface reaction[32]. The input configuration-energy database contains ~10^5 DFT total energies for equilibrium and distorted configurations of CH_4 interacting on the static distorted Ni (111) surface. Most of them are selected from quasi-classical trajectory calculations based on the preliminary version of PES. Configurations for the static distorted surface with the fixed DOF Q are extracted from a Boltzmann temperature sampling. More details about the DFT electronic structure calculations and the NN method as well as the fitting procedure can be found in the Supplemental Material.

The 8D quantum model Hamiltonian for the CH_4 dissociation on the fixed top Ni atom of the static distorted Ni(111) surface in the Jacobi coordinates $V(R,r,s,\chi,\theta_1,\varphi_1,\theta_2,\varphi_2;Q)$ shown in Fig.1 can be written as

$$H = -\frac{1}{2\mu_R}\frac{\partial^2}{\partial R^2} - \frac{1}{2\mu_r}\frac{\partial^2}{\partial r^2} + \frac{l^2}{2\mu_r r^2} + K_{CH_3}^{vib}$$
$$+K_{CH_3}^{rot} + V(R,r,s,\chi,\theta_1,\varphi_1,\theta_2,\varphi_2;Q) \qquad (1)$$

where μ_R and μ_r are the mass of CH_4 and reduced mass of H-CH_3, R is the distance from the center of mass of CH_4 to the surface, r is the distance from the center of mass of CH_3 to H, s is the bond length of CH bond in CH_3, χ is the angle between a CH bond and the C_{3v} symmetry axis of CH_3. As we know, because of this important C_{3v} symmetry restriction, the DOFs of CH_3 will be reduced from 6 to 2 if one chooses the bond length and umbrella angle as the coordinates. In this work we have fixed the CH bond length in the CH_3 group because it almost does not change in all the TS geometries[23]. Therefore the DOF of s in the CH_3 can be ignored to reduce computation. The DOF of azimuth on the targeted top site is neglected also. We define the bending angle between vectors R and r to be θ_1; φ_1 is the azimuth angle of the rotation of HCH_3 around the vector r; θ_2 is the bending angle between vectors r and s; φ_2 is the azimuth angle of the rotation of CH_3 around the vector s. The first two terms in Eq.1 are the kinetic energy operators for R and r, respectively, and l is the orbital angular momentum operator of atom H with respect to CH_3. $K_{CH_3}^{vib}$ and $K_{CH_3}^{rot}$ are the vibrational and rotational kinetic energy operators of CH_3, respectively. No vibration-rotation coupling exists due to the symmetry requirement and the definition of the CH_3-fixed frame. Q is the DOF of the targeted lattice vibration in Z direction. In this work, we choose several fixed Q values to represent the lattice vibration. For more details about our 8D quantum model, we refer to our group's work in the X+ YCZ_3 reaction systems[33,34].

A full description of the initial wave function and tests of accuracy (including comparisons of the geometries and energies of six transition states[23] on some static distorted Ni (111) surfaces predicted from the PES and DFT calculations) will be presented elsewhere. Here we simply mention that the time-dependent Schrodinger equation was solved using the split-operator method, with an initial Gaussian wave packet. The sticking probability S_0 is obtained at a dividing surface placed at r=1.85 Å using a flux formalism, and it is not multiplied by a factor of four[35]. Our 14D-PES reproduces very well those DFT results, with the root mean square errors (RMSE) being only 5.4 meV for the entrance region and 14.4 meV for the interaction and product regions, respectively. The discrepancies of the dissociating CH bond length R_{CH} (< 0.05 Å) and the activation energies E_{TS} (< 20 meV) at six TSs are very small.

3. Results and Discussions

Based on this highly accurate PES, quantum dynamics calculations using our 8D quantum model have been carried out for GS CH_4 dissociation on the fixed top site of different static distorted Ni(111) surfaces, i.e., with different fixed *Q* values. Fig. 2 shows the sticking probability S_0 as a function of the normal incident energy E_i, for seven *Q* values which are respectively 0.25 Å, 0.15 Å, 0.05 Å, 0.00 Å, -0.05 Å, -0.15 Å, -0.25 Å. As seen from Fig. 2, for each fixed *Q* value, the S_0 of GS CH_4 increases exponentially as the E_i increases in the low energy region. Furthermore, the S_0 decreases rapidly as *Q* varies from positive values to negative values. In principle, for positive *Q*, i.e., upward displacement of the Ni atom, the puckering effect would decrease the activation barrier of molecule dissociation and thus increases its sticking probability. In contrast, the recoiling effect of the lattice Ni atom into bulk phase (for negative *Q*) would increase the activation barrier and thus decrease the sticking probability. Our quantum dynamics results have unambiguously demonstrated this tendency. It is noted also that on these static distorted surfaces, the slopes and asymptotes of the S_0 curves of GS CH_4 are very similar. This provides qualitative evidence for the applicability of the energy-shifting scheme to polyatomic molecular gas-surface reactions.

We next demonstrate how to achieve quantitative agreement with the quantum treatment through the energy-shifting procedure[24]. In the energy-shifting scheme, the energy-resolved sticking probability S_0 would be obtained by shifting the given S_0 along the energy axis with the corresponding energy. Thus, the shifting energy from our quantum dynamics calculations (label it as quantum model) on each *Q* is obtained as the averaged shifting energies which refer to three given S_0 (i.e., 10^{-2}, 10^{-3} and 10^{-4}) at Q=0. The relationship of the shifting energy as a function of *Q* from the quantum model is shown in Fig. 3 together with the linear model[24] as well as our new model presented below. It is worth noting that the shifting energy in the negative *Q* region decreases more strongly than it increases in the positive *Q* region. In order to understand this non-linear effect in-depth and to gain some insight into its relationship with the anharmonicity, we present the following investigations.

Due to the exponential dependence of S_0 on the normal incident energy E_i, the value of the shifting energy has a dramatic effect on S_0 particularly in the region of low E_i. In the linear model proposed by Jackson's group, the shifting energy is modeled as βQ. The quantum dynamics results agree very well with this linear model in the region of small *Q* (i.e., -0.1 Å $< Q < 0.1$ Å) in Fig. 3. However, it is clear that the shifting energy from the quantum calculations becomes lower than that from the linear model in the region of larger *Q* (i.e., $Q < -0.1$ Å and $Q > 0.1$ Å). Moreover, the difference in the shifting energy between the quantum model and the linear model rapidly increases as *Q* increases. This indicates that the energy-shifting in the present system has a nonlinear relationship with the displacement of the lattice atom.

In order to improve on the linear model, we include some important factors that contribute to the dependence of the shifting energy on *Q*. One basic assumption for applying the energy-shifting scheme to obtain the S_0 is that the PES topology and TS geometries should be independent of Q. Actually, these are different due to the strength of electronic couplings between the dissociating molecule and the substrate. We will lift this limitation by explicitly including these effects in an improved model of the shifting energy. Specifically, we propose the shifting energy to include the potential energy of the lattice vibration itself as well as the change of the activation barrier at the TSs. The shifting energy, $\delta E(Q)$, with respect to Q, can be proposed as:

$$\delta E(\mathrm{Q}) = V_{TS}(\mathrm{Q}=0) - V_{TS}(\mathrm{Q}) \tag{2}$$

where $V_{TS}(Q=0)$ is the activation barrier at the TSs on a static flat surface, $V_{TS}(Q)$ is the activation barrier at the TSs on Q. The corresponding reference systems are those CH_4 far from these static distorted surfaces.

The variation of activation barrier at the TSs is thus taken into account from the PES and directly from DFT calculations. This effect on the shifting energies is respectively illustrated in Fig. 3 with VTS_{PES} correction and VTS_{DFT} correction, albeit without relaxing the TSs geometries. Our highly accurate PES can give much closed values to the DFT results. Nevertheless, the contribution of the variation of activation barrier at the TSs overestimates the shifting energy in the negative Q region and underestimates it in the positive Q region. Accordingly, it still does not yield good descriptions of the relationship in the larger Q (i.e., $Q < -0.2$ Å and $Q > 0.2$ Å), even if good agreement starts in the region of Q from -0.2 Å to 0.2 Å.

To further improve agreement with the quantum model, it is necessary to consider the relaxation of the TSs geometries for each Q when accounting for the effect of the variation of activation barrier at the TSs. We label it as VTSR model in Fig. 3. After optimizing the geometries of the TSs for each Q based on our 14D PES, finally, this correction yields the same relationship of the shifting energy and Q as the quantum model does. More significantly, this additional relaxation effect of the TSs not only gives excellent agreement in the small Q region, but also does so very well in the large Q region. Consequently, the shifting energy obtained from quantum dynamics calculations can be precisely reproduced from our VTSR model using *ab initio* methods.

Here we mention that our DFT calculations are very identical to those done in the approach of Jackson and co-workers[36]. That is to locate the transition state configuration for several fixed values of Q, and then the molecule is fully relaxed at the transition state for each Q. The shifting energy is then given by Eq. (2). The error in the Jackson linear approach is that these DFT calculations are typically done for one TS configuration with relatively small values of Q, and then the shifting energy which is fit to these DFT values is assumed to be linear[36]. Due to only considering small values of Q (less than or equal to 0.15 Å), non-linear variations of the shifting energy with Q are neglected. Moreover, our results suggest that the importance of relaxation for each Q should be considered for all six possible transition states configurations of CH_4/Ni(111) system. If the correct nonlinear relationship of the shifting energy with the lattice vibration displacement Q were used, one can get very accurate results as quantum dynamics gives.

By scrutinizing the influence of these corrections on the shifting energy, we define the correction energy $\delta E_C(Q)$ as the difference between the improved models and the linear model. From inset of Fig.3, the strong Q-dependence of these corrections is demonstrated for the $\delta E_C(Q)$. For instance, at Q= -0.35 Å (or 0.35 Å), the correction energy between the quantum model and the linear model is about 100 meV (or 50 meV). Such large discrepancy would directly affect the sticking probability of CH_4 in the low normal incident energy region if ones apply the energy-shifting scheme for high surface temperatures.

Fig. 4 shows the sticking probability S_0 of GS CH_4 from three different models (i.e., linear model, sudden-quantum model, and our VTSR model) for three surface temperatures: 90K, 475K and 1200K. Compared with the S_0 on the top site at the equilibrium position (Q=0), ones can note that, the surface temperature has an important effect on the S_0 particularly in the low normal incident energy region. In good agreement with that reported by Jackson's group[20,21], the linear model, the sudden-quantum model and the VTSR model can give similar results at low surface temperature of 90K. When increasing the surface temperature to 475K, however, the difference between the sudden-quantum model and the linear model becomes obvious, but the new VTSR model can still keep in nice agreement with the sudden-quantum model. Even at much higher surface temperature of 1200K, it gives excellent agreement with sudden-quantum model in the region of low E_i, whereas the S_0 obtained from the linear model is lower than that from the sudden-quantum model, e.g., about 5 times lower at the normal incident energy of 0.6 eV.

4. Conclusions

In summary, we have presented the results of quantum dynamics study of lattice thermal motion through simulations of GS CH_4 dissociation on the fixed top site of some static distorted Ni(111) surfaces. Based on a highly accurate 14D PES, our quantum dynamics simulations provide quantitative evidence for the applicability of the energy-shifting scheme to polyatomic molecular gas-surface reactions. Through analysis of the discrepancies between the full quantum treatment and the linear model, we have developed the new VTSR model that not only reproduces the quantum results at low temperatures but also works very well at high temperatures. This model goes beyond a fit of the observed energy shifting and explains it as a result of the intrinsic contributions derived from the physical potential of the system. With the VTSR model, the sticking probability for surface temperatures may be precisely obtained from a single quantum dynamics calculation on a PES of the static flat surface with a nonlinear energy shifting scheme according to Eq. 2 .The required data for Eq. 2 may be calculated directly from the computationally cheap DFT method for the TS relaxation dependant on the lattice coordinate *Q*. With its accuracy and efficiency demonstrated in this work, we hope our VTSR model can provide a very useful strategy for studying lattice effects on gas-surface reactions for quantum dynamics calculations and be applicable to recent investigations of H_2O dissociation on metal surfaces.

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Figure captions

Fig. 1(color online) Eight-dimensional Jacobi coordinates for quantum dynamics simulations of CH_4 interacting on Ni (111) surface.

Fig. 2(color online) Sticking probability S_0 of GS CH_4 impinging on the fixed top site of static distorted Ni(111) surfaces with seven fixed Q values: dashed lines represent positive Q (in Å) values and solid lines represent negative Q (in Å) values.

Fig. 3(color online) Shifting energy $\delta E(Q)$ using different models as a function of Q. Inset figure represents the correction energy $\delta E_C(Q)$ using different models as a function of Q.

Fig. 4(color online) Sticking probability S_0 of GS CH_4 impinging on a top site of Ni(111) as a function of E_i for different surface temperatures: 90K, 475K and 1200K. Solid black line represents results on the static flat surface (Q=0), solid red lines represent results from the linear model, solid green lines represent results from the quantum model, dashed blue lines represent results from the VTSR model.

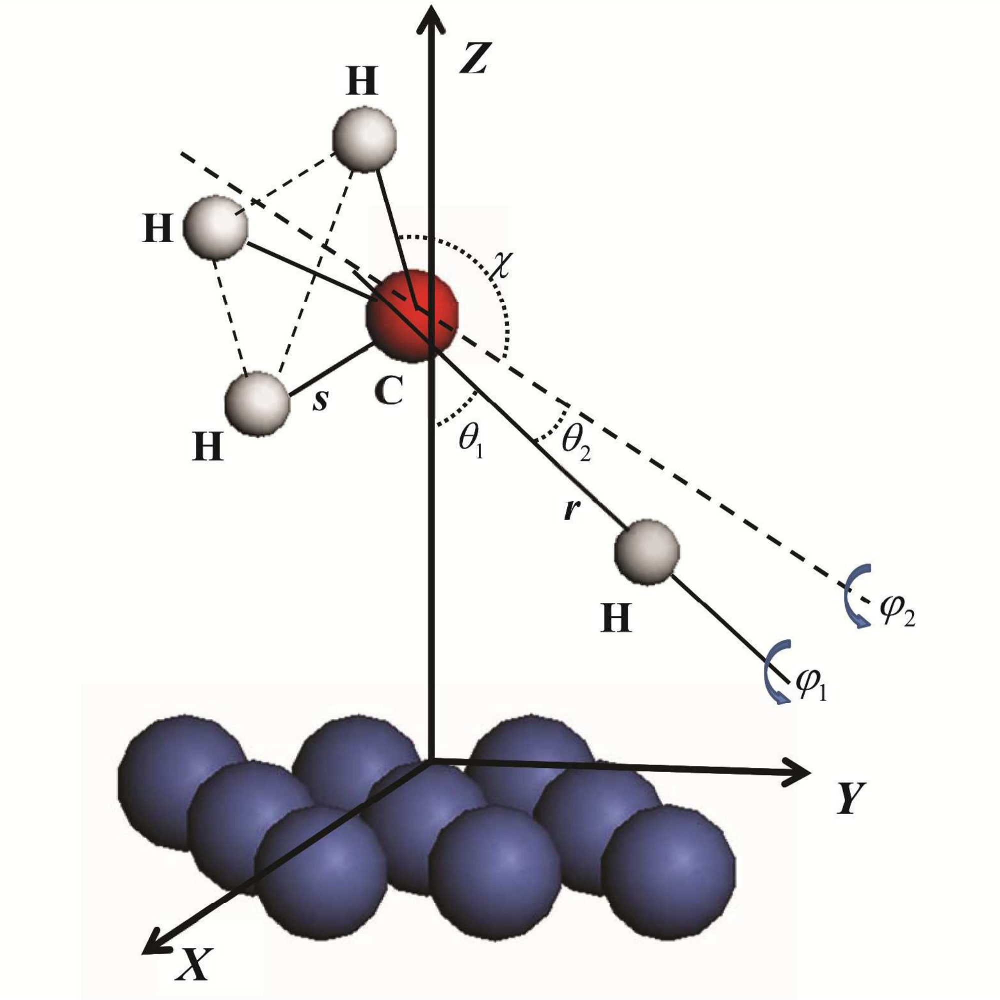

Fig.1 Shen et al

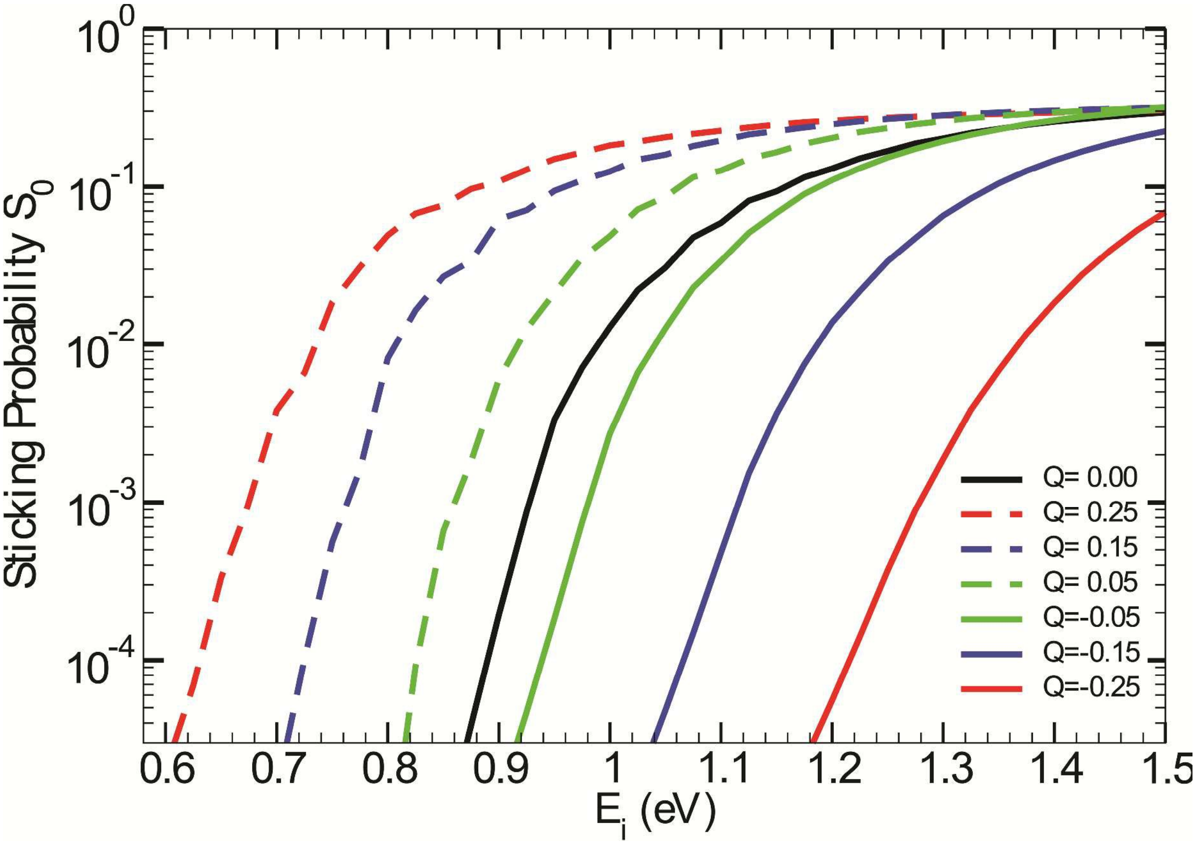

Fig.2 Shen et al

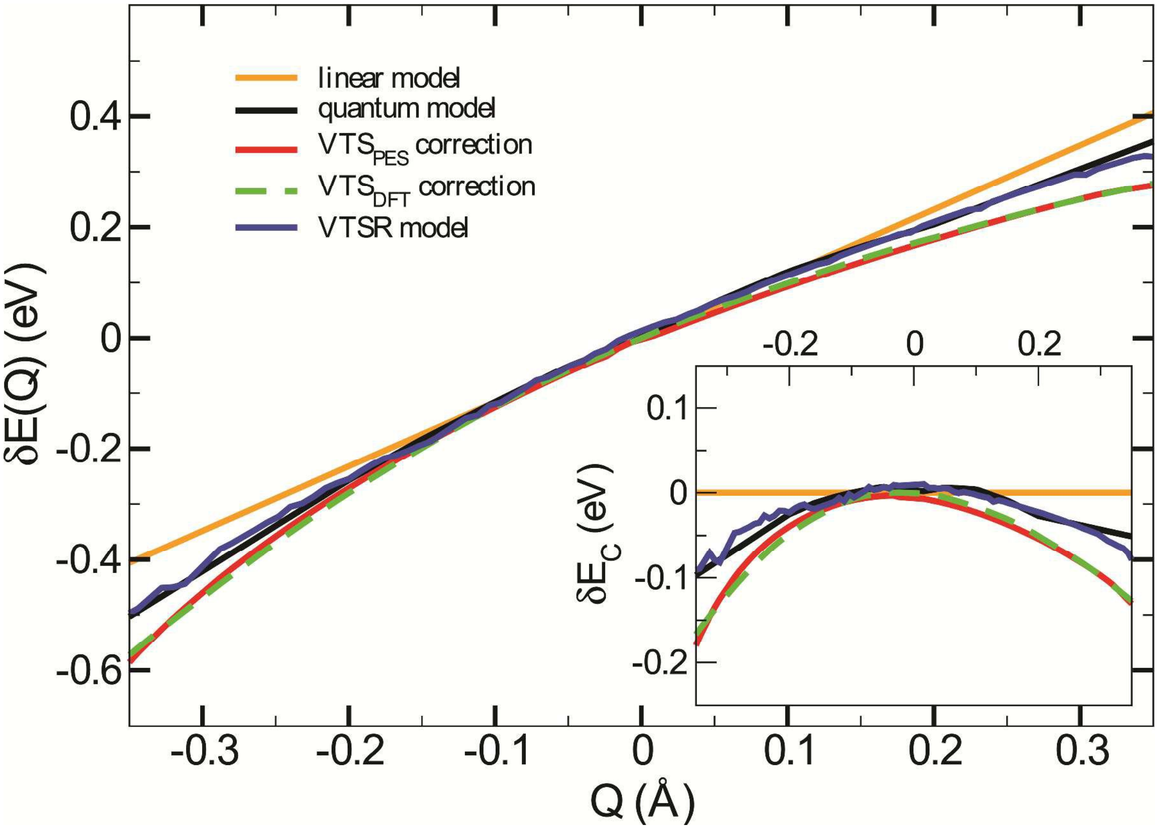

Fig. 3 Shen et al

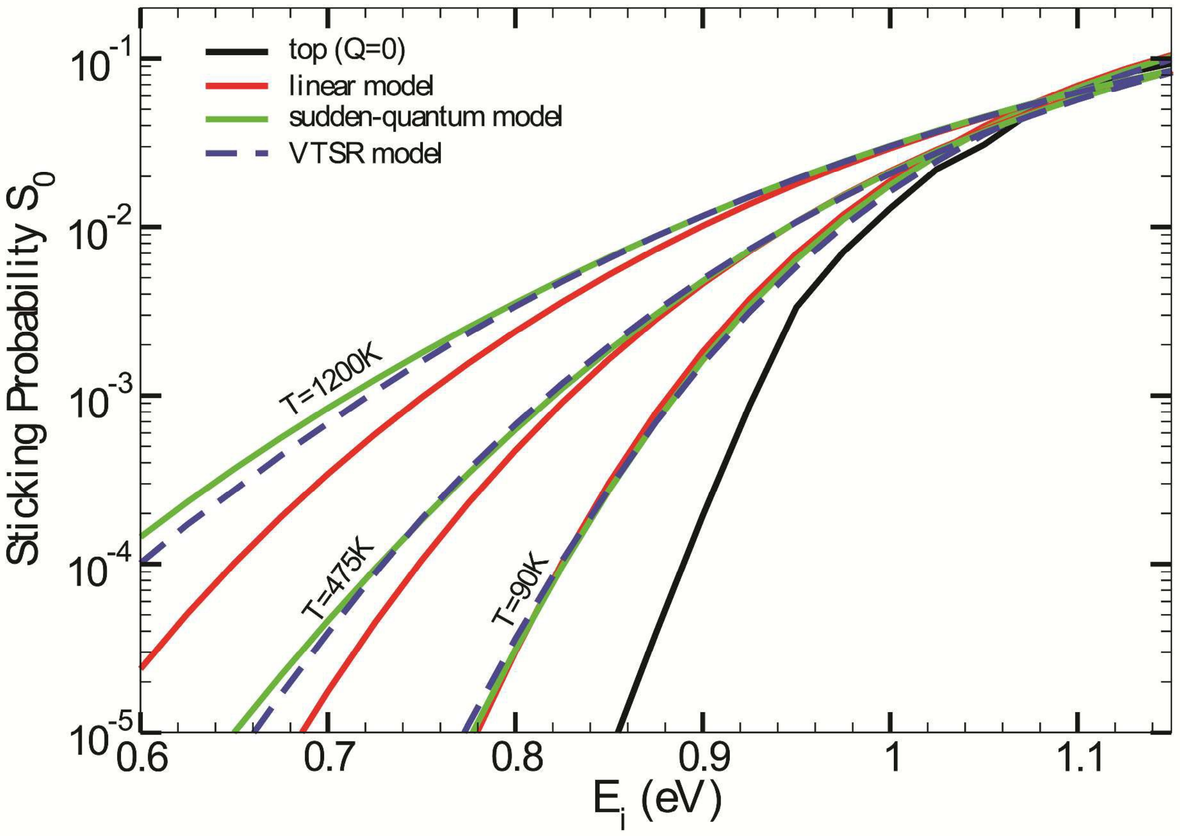

Fig. 4 Shen et al

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