Ab Initio Simulations of the Kinetic Properties of the Hydrogen Monomer on Graphene†

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The understanding of the kinetic properties of hydrogen (isotopes) adatoms on graphene is important in many fields. The kinetic properties of hydrogen-isotope (H, D, and T) monomers were simulated using a composite method consisting of density functional theory, density functional perturbation theory, and harmonic transition state theory. The kinetic changes of the magnetic property and the aromatic π bond of the hydrogenated graphene during the desorption and diffusion of the hydrogen monomer were discussed. The vibrational zero-point energy corrections in the activation energies were found to be significant ranging from 0.072 to 0.205 eV. The results obtained from quantum mechanically modified harmonic transition state theory were compared with the ones obtained from classical-limit harmonic transition state theory over a wide temperature range. The phonon spectra of hydrogenated graphene were used to closely explain the (reversed) isotope effects in the prefactor, the activation energy, and the jump frequency of the hydrogen monomer. The kinetic properties of the hydrogen-isotope monomers were simulated under conditions of annealing for 10 min and of heating at a constant rate (1.0 K/s). The isotope effect was observed; that is, a hydrogen monomer of lower mass is desorbed and diffuses more easily (with lower activation energies). The results presented herein are very similar to other reported experimental observations. This study of the kinetic properties of the hydrogen monomer and many other involved implicit mechanisms provides a better understanding of the interaction between hydrogen and graphene.

I. Introduction

The fact that hydrogen interacts with graphite surface in outer space1–4 and in fusion devices5–7 requires a clear understanding of the kinetic properties of hydrogen adatoms on graphite surfaces for astronomy and the nuclear industry. Such properties are also very important for the realization of both graphene-based hydrogen storage8 and graphene-based electronics.9–15

The desorption and diffusion of hydrogen adatoms on graphite surfaces are two important kinetic processes whose properties depend sensitively on the interaction between the adatom and the graphite surface. Consequently, investigation of the desorption and diffusion of hydrogen adatoms on graphite surfaces can further our understanding of the mechanisms involved in these interactions. Some research has been carried out on the kinetic properties of hydrogen adatoms on graphite surfaces.2,3,16,17 The adsorption of hydrogen monomers on graphene is an essential step in hydrogenation, and the kinetic properties of this step determine the outcome of the hydrogenation process. Hornekaer et al. found that a large fraction of the D monomers on a graphite surface will be desorbed during annealing at room temperature for 10 min, while the D monomers on the graphite surface are diffusionally immobile at room temperature.3 Such diffusional immobility is consistent with Baulouche’s observations in time-programmed desorption experiments.18 Some theoretical studies on the kinetic properties of hydrogen monomers have also been reported.3,4,19–22 The calculated chemisorption energies of hydrogen monomer on graphene vary around a value of 0.75 eV with a range of about 0.3 eV; this magnitude of variation represents quite a large energetic uncertainty in kinetics. Furthermore, in kinetic simulations, the vibrational characteristics of the light-mass hydrogen monomers should be considered. Thus, a fully theoretical simulation that can be precisely and directly compared with experimental observations in both desorption and diffusion is still lacking.

In this report, the kinetic properties of various hydrogen-isotope (H, D, and T) monomers were simulated by means of a composite method consisting of density functional theory (DFT),23 density functional perturbation theory (DFPT),24 and harmonic transition state theory (hTST).25–28 The kinetic change of the magnetic property of the hydrogenated graphene during the desorption and diffusion of the hydrogen monomer was discussed. The vibrational contribution, including the zero-point energy correction in the activation energy, was considered with hTST. The kinetic properties of various hydrogen-isotope monomers were simulated under conditions of annealing for 10 min and of heating at a constant rate (1.0 K/s).

II. Methodology

The overbarrier jump frequency between two local minimum states (initial and final states or reactant and product states) can be expressed in the Arrhenius form as:27,29

\[ \nu = \nu^* \exp \left( - \frac{E_{ac}}{k_B T} \right) \tag{1} \]

where \( \nu^* \) is the exponential prefactor and \( E_{ac} \) is the activation energy that is required for the reaction to occur. The activation
energy is defined herein to be the vibrational zero-point energy corrected potential barrier, which is expressed as

\[ E_{ac} = \Delta E_p + \frac{1}{2} \sum_{i=1}^{3N-1} \hbar \omega_i^f - \frac{1}{2} \sum_{i=1}^{3N} \hbar \omega_i^s \]

\[ = \Delta E_p - \Delta F_{vib}(0) \quad \text{(2)} \]

where \( \Delta E_p \) is the potential barrier in the reaction path, which can be obtained from DFT calculations, and \( \omega_i^f \) and \( \omega_i^s \) are the vibrational frequencies of the \( i \)th mode in the initial and saddle-point states, respectively. Correction \( \Delta F_{vib}(0) \) comes from the vibrational zero-point energy difference between the initial and saddle-point states. The total vibrational degrees of freedom are \( 3N \); an imaginary vibrational mode along the migration coordinate in the saddle-point state is excluded; thus, \( 3N - 1 \) vibrational modes are considered for the saddle-point state. From quantum mechanically modified hTST, prefactor is expressed as\(^\text{25,29,30}\)

\[ \nu_{qm} = \frac{k_B T}{\hbar} \prod_{i=1}^{3N-1} \left[ 1 - \exp \left( - \frac{\hbar \omega_i^f}{k_B T} \right) \right] \]

\[ \times \frac{k_B T}{\hbar} \prod_{i=1}^{3N} \exp \left( \frac{\hbar \omega_i^s}{k_B T} \right) \tilde{n}_T(\omega_i^s) \]

\[ \approx \frac{k_B T}{\hbar} \prod_{i=1}^{3N-1} \left( 1 - \exp \left( - \frac{\hbar \omega_i^f}{k_B T} \right) \right) \tilde{n}_T(\omega_i^f) \quad \text{(3)} \]

where \( \tilde{n}_T(\omega_i) \) is the bosonic phonon occupation number of the \( i \)th vibrational mode. When the temperature approaches infinity, the classical limit of the prefactor is expressed as

\[ \nu_{cl} = \frac{1}{2\pi} \prod_{i=1}^{3N-1} \omega_i^f \quad \text{(4)} \]

This classical-limit form is also the Vineyard’s form\(^\text{26}\) in which all of the vibrational modes are assumed to be completely thermoactived. From hTST as described above, the mass-dependent vibrational frequencies are responsible for the difference in kinetic properties of H, D, and T monomers as shown later in this report.

The first-order rate equation for desorption can be expressed as\(^\text{18,27}\)

\[ \frac{dn(t)}{dt} = - \nu_{des}(T)n(t) \quad \text{(5)} \]

where \( \nu_{des} \) is the desorption frequency, \( n(t) \) is the residual number of hydrogen monomers on graphene at the \( t \) moment, and \( t = 0 \) represents the starting moment for initializing the kinetic movement.

In the annealing process, the temperature is kept constant \( (T = T_0) \); in that case, the variation of the residual number with respect to time is expressed as

\[ n(t) = n(0) \exp[- \nu_{des}(T_0) t] \quad \text{(6)} \]

The diffusion can be described by the mean square displacement \( \langle (\mathbf{r}(t) - \mathbf{r}(0))^2 \rangle \) of a monomer parallel to graphene. From Fick’s second law, we have

\[ \langle \mathbf{r}(t) - \mathbf{r}(0) \rangle^2 = 2dD_{ad}(T)t \quad \text{(7)} \]

where \( d \) is the dimensionality of the diffusion of a hydrogen monomer on graphene (2 here), and \( D_{ad} \) is the diffusion coefficient, which is temperature-dependent and is expressed as\(^\text{29}\)

\[ D_{ad} = \frac{1}{2d} \Gamma a^2 \quad \text{(8)} \]

which can be used directly to determine whether the hydrogen monomer on graphene is diffusionaly mobile.

In the heating process, if the temperature increases at a constant rate \( \alpha (T = \alpha t) \), the variation of the residual number with respect to time is expressed as

\[ n(t) = n(0) \exp\left[- \int_0^t \nu_{des}(\alpha t) \, dt \right] \quad \text{(10)} \]

where \( \alpha \) is always 1.0 K/s.\(^\text{2,16,17}\) The relative desorption rate is therefore defined by the ratio of the desorption rate to the initial monomer number

\[ R_{des}(T, t) = \frac{\nu_{des}(T)n(t)}{n(0)} \quad \text{(11)} \]

which is both time- and temperature-dependent.

In this report, a monolayer of graphene served as a structural model of a graphite surface. This was feasible because the effect of the weak van der Waals interaction between neighboring graphene layers on the chemisorption properties of hydrogen monomer can be neglected; in our DFT tests using local density approximation (LDA) and generalized gradient approximation (GGA), the bilayer-graphene structural model yields potential barriers with a difference less than 8 meV with respect to the monolayer structural model. The lattice constant of graphene has been found to be very close to graphite (within 0.05%) at 200–500 K,\(^\text{31}\) which is the most important temperature range for the kinetic movements of the hydrogen monomer as shown below. A hydrogen monomer on a \( 5 \times 5 \) periodic supercell of graphene (50 C atoms) with a 10 Å vacuum along the direction perpendicular to the surface can be considered as an isolated monomer; our tests show that the interaction between two monomers in two such neighboring supercells can be neglected.
calculation of electronic density of states (DOS), a $6 \times 4 \times 1$ uniform $k$-point grid with the tetrahedron interpolation scheme was used for the integration of the electronic states over the first Brillouin zone. For the other calculations, a $4 \times 4 \times 1$ uniform $k$-point grid with the Methfessel-Paxton smearing potentials were used to describe the electronic exchange and correlation energy. The wave function and the charge density were expanded using energy cutoffs of 35 and 350 Ry. For the calculation of electronic density of states (DOS), a $6 \times 6 \times 1$ uniform $k$-point grid with the tetrahedron interpolation scheme was used for the integration of the electronic states over the first Brillouin zone. For the other calculations, a $4 \times 4 \times 1$ uniform $k$-point grid with the Methfessel-Paxton smearing technique was used, where the smearing width was 0.03 Ry. The partial DOS of hydrogen was obtained using the Löwdin population analysis. A force threshold of $10^{-4}$ Ry/bohr was used for the structural optimization. The reaction paths were described by the minimum energy paths (MEPs) between two local minimum states that were calculated using the climbing-image nudged elastic band method with five images for each reaction path. For calculating the vibrational frequencies, only the gamma point at the Brillouin zone center was selected.

III. Results and Discussion

The calculated MEPs for the desorption and diffusion processes of a hydrogen monomer are shown in Figure 1 in which the structures of the initial (reactant), saddle-point (transition), and final (product) states are also shown. The final state in the desorption MEP has been fixed to the physisorption state. The yellow spheres represent carbon atoms and the smaller blue spheres represent hydrogen atoms.

Figure 1. MEPs for the (a) desorption and (b) diffusion of a hydrogen monomer on a graphene layer. In the paths, the initial, saddle-point, and final states are labeled with stars, and their structures are shown at the side of the figure. The final state in the desorption MEP is fixed to be the physisorption state. The yellow spheres represent carbon atoms and the smaller blue spheres represent hydrogen atoms.

(see the Supporting Information). This is consistent both with the findings of Shytov on the basis of a theory of electron-mediated interaction and with those of Boukhvalov and Katsnelson on the basis of DFT calculations. The DFT and DFPT calculations were carried out using the Quantum Espresso code package in which the ultrasoft spin-polarized PBE pseudopotentials were used to describe the electronic exchange and correlation energy. The wave function and the charge density were expanded using energy cutoffs of 35 and 350 Ry. For the calculation of electronic density of states (DOS), a $6 \times 6 \times 1$ uniform $k$-point grid with the tetrahedron interpolation scheme was used for the integration of the electronic states over the first Brillouin zone. For the other calculations, a $4 \times 4 \times 1$ uniform $k$-point grid with the Methfessel-Paxton smearing technique was used, where the smearing width was 0.03 Ry. The partial DOS of hydrogen was obtained using the Löwdin population analysis. A force threshold of $10^{-4}$ Ry/bohr was used for the structural optimization. The reaction paths were described by the minimum energy paths (MEPs) between two local minimum states that were calculated using the climbing-image nudged elastic band method with five images for each reaction path. For calculating the vibrational frequencies, only the gamma point at the Brillouin zone center was selected.

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In the desorption saddle-point state, the hydrogen atom is at the top site with a height of 1.98 Å. The potential barrier was defined as the energy difference between the saddle-point state and the initial state; the calculated desorption potential barrier is 1.075 eV. The final (physisorption) state is 0.865 eV higher in energy than the initial (chemisorption) state; the fully desorbed state is 0.890 eV higher than the initial state and 0.035 eV higher than the physisorption state. The small energy difference of 0.035 eV also indicates that a very large vacuum is needed if one wants to obtain the fully desorbed state in the vacuum. This calculated potential surface along the desorption MEP is very close to Hornekær et al.’s theoretical result, where the smoothly varying potential surface for the MEP from the physisorption state to the fully desorbed state also has been shown. In addition, if the hydrogen monomer climbs over the desorption barrier, it will escape from the graphene layer with high velocity after climbing down the potential barrier. In the diffusion process shown in Figure 1b, the hydrogen atom moves along a C–C bond at an average height of about 1.40 Å. In the diffusion saddle-point state, the hydrogen atom is at the bridge site with a height of 1.20 Å. The diffusion potential barrier is 1.035 eV, which is somewhat smaller than the desorption potential barrier. This potential barrier tends to be insensitive to the supercell size in our calculation (see the Supporting Information), although there has been discussion on this point recently.

The kinetic movement of the hydrogen monomer can result in the kinetic change of the magnetic property of the hydrogenated graphene. Figure 2 shows the electronic DOS of the initial, desorption saddle-point, and diffusion saddle-point states as well as the respective partial DOS of the hydrogen monomer. The initial state and the desorption saddle-point state both have a total magnetic moment of 1.0 $\mu_B$, while the diffusion saddle-point state is nonmagnetic. The DOS of the initial state is consistent with the theoretical results by others. The adsorption of hydrogen atom breaks an aromatic $\pi$ bond in graphene, which results in one unsaturated C(p) orbital. This unsaturated C(p) orbital is responsible for the two narrow peaks (bands) placed around the Fermi level in the total DOS. The energy gap is 0.245 eV. As seen from the partial DOS of the H(1s) orbital, the contribution from the H(1s) orbital to these two bands is small. The unpaired electron occupying the lower band is responsible for the magnetic moment of 1.0 $\mu_B$. The energies of the other spin-up bands shift downward a little with respect to their spin-down counterparts because of the exchange-correlation interaction between the electrons in the magnetic C(p) orbital and the other electrons. In the desorption saddle-point state, the partial DOS of the H(1s) orbital is much larger than that in the initial state. This is because the H(1s) orbital is much less hybridized with graphene in the desorption saddle-point state than that in the initial state, and less electrons transfer from H to graphene. Thus, in the desorption process, the
The displacement of the hydrogen monomer in each eigenvector of the vibrational dynamic matrix was represented by $e^{i\omega_i} (i$ is the index of the vibrational mode); the calculated spectra of the $|e^{i\omega_i}|^2$ ($M = H, D,$ and $T$) for the initial, desorption saddle-point, and diffusion saddle-point states are shown in Figure 3. The modes with large values of $|e^{i\omega_i}|^2$ are localized stretching ($S$) and bending ($B$) modes. The isotope effect in the phonon spectra is obvious in that the vibrational frequencies of hydrogen monomers as shown in the second paragraph below. In addition, the real stretching and bending modes in the desorption saddle-point state have larger vibrational frequencies than the real bending modes in the desorption saddle-point state; this will result in a difference between the exponential prefactor of desorption and that of diffusion as shown in the next paragraph. For light-mass atoms such as hydrogen isotopes, the vibrational zero-point energy corrections ($\Delta F_{vib}^{(0)}$) are very important to the precise estimation of activation energies. The calculated $\Delta F_{vib}^{(0)}$ values for $H$, $D$, and $T$ monomers are listed in Table 1. The values, which range from 0.072 to 0.205 eV, indeed cannot be neglected if the kinetic properties of hydrogen isotope monomers are to be understood. The isotope effect in the $\Delta F_{vib}^{(0)}$ values, which shows that $\Delta F_{vib}^{(0)}$ decreases with increasing monomer mass, is a result of the isotope effect in the phonon spectra. Both of these isotope effects will result in the presence of an isotope effect in the desorption and diffusion frequencies of hydrogen monomers as shown in the second paragraph below. In addition, the $\Delta F_{vib}^{(0)}$ correction for the desorption potential barrier is larger than that for the diffusion potential barrier because of the disappearance of the highest-frequency real stretching modes and the significant lowering of the bending modes in the desorption saddle-point state with respect to those modes in the initial state. However, in the diffusion saddle-point state, only one lower-frequency real bending mode disappears, and the real stretching and bending modes are less affected. The resonant in-band modes (modes with small values of $|e^{i\omega_i}|^2$ in these three states are slightly shifted and are nearly independent of the isotopic character of the adatom. The mode with a frequency around 630 cm$^{-1}$ observed in experiments is an example of the resonant in-band modes.$^{17,47}$

The exponential prefactors for $H$, $D$, and $T$ monomers calculated from the quantum mechanically modified hTST ($\tau_{\text{q}}^{\text{hSS}}$) and its classical limit ($\tau_{\text{c}}^{\text{hSS}}$, the Vineyard form$^{26}$) are shown in

![Figure 3](image-url)
in the classical-limit hTST, all vibrational modes are regarded as prefactors should be equal at very high temperatures. In the quantum mechanically modified hTST because of the high-frequency localized modes are fully considered in the localized stretching and bending modes, the contributions from hydrogen monomer prefactors are mainly determined by the relationship as discussed in the previous paragraph. However, among the quantum mechanically modified diffusion prefactors, the relationship \( v_{qm}^* (T) > v_{qm}^* (D) > v_{qm}^* (H) \) holds, and the isotope effect is reversed with respect to the isotope effect in the \( v_{cl}^* \)'s. The values of the quantum mechanically modified diffusion prefactors for H, D, and T monomers are nearly the same over a very wide temperature range (0–1000 K). This can be understood from eq 3 and the phonon spectra in Figure 3. For convenience, the phonon spectra are divided into lower and higher regions below and above 500 cm\(^{-1}\), respectively. In the initial state, all the localized modes are in the higher region. The real localized bending modes in the desorption saddle-point state are significantly lowered such that they now fall within the lower region, while the real localized modes in the diffusion saddle-point state remain in the higher region. In the plotted temperature range, the \( v_{qm}^* \)'s are mainly determined by the vibrational modes in the lower region because of the large bosonic phonon occupation numbers of these modes. In the phonon spectra of the initial and diffusion saddle-point state, the lower region contains only the resonant in-band modes, which are nearly independent of the isotopic character of the monomer, therefore, the \( v_{qm}^* \)'s for H, D, and T monomers in diffusion are nearly the same. However, in the phonon spectra of the desorption saddle-point state, the low-lying localized bending modes are significantly occupied by phonons at temperatures above 100 K; in this state, the localized modes for the T monomer are the lowest and should be occupied by most phonons and are most readily thermoactivated followed by the modes for D and H monomers in that order. This order of thermoactivation leads to the relative magnitude order of the \( v_{qm}^* \)'s for H, D, and T monomers at temperatures above 100 K; however, this magnitude order will be progressively altered as the temperature increases to high values (not shown) finally achieving the same order as \( v_{cl}^* \)'s.

The desorption frequencies \( (v_{des}) \) and diffusion frequencies \( (v_{diff}) \) for the hydrogen-isotope monomers are shown in Figure 5, where the \( v_{qm}^* \) is used as the prefactor. Both \( v_{des} \) and \( v_{diff} \) decrease with increasing monomer mass. This isotope effect is due to the isotope effect in the vibrational zero-point energy correction as shown in Table 1. The \( v \) is exponentially dependent on the activation energy and linearly dependent on the \( v_{qm}^* \); thus, the small reversed isotope effect in the \( v_{qm}^* \)'s for the desorption (Figure 4a) does not compete with the normal isotope effect in the zero-point energy corrections. For each isotope, the desorption frequencies are larger than the corresponding diffusion frequencies because the desorption activation energy is less than the diffusion activation energy from eq 2. Additionally, the desorption prefactor is also larger than the diffusion prefactor.

At room temperature (298 K), the \( v_{des} \)'s for H, D, and T monomers are 1.6 × 10\(^{-3}\), 4.8 × 10\(^{-4}\), and 3.0 × 10\(^{-4}\) s\(^{-1}\), respectively; the \( v_{des} \)'s are 1.4 × 10\(^{-2}\), 1.4 × 10\(^{-3}\), and 5.5 × 10\(^{-4}\) s\(^{-1}\), respectively.

After several hydrogen monomers are deposited onto a graphene or graphite surface and if the system is annealed at a constant temperature \( T_0 \) for a time interval \( t_0 \), the monomers are desorbed from the surface or diffuse away from the initial site. The kinetic properties of hydrogen monomers under this annealing condition were simulated by eqs 6 and 9 with \( t_0 \) being 10 min (600 s) in accordance with Hornekær et al.’s experiment. Figure 6a shows the variations of the relative residual monomer number \( (n(n_{0})) / n(n_{0}) \) and the diffusion radius \( (r_{diff}) \) with respect to \( T_0 \). The curves of \( n(n_{0}) / n(n_{0}) \) and \( r_{diff} \) present an isotope effect that a hydrogen monomer of lower mass is desorbed from the surface and diffuses on the surface more easily. During a 10 min annealing, significant desorption does not occur in our simulation until \( T_0 > 250 \) K. However, the monomers are nearly completely desorbed at \( T_0 > 294 \) K for H, at \( T_0 > 312 \) K for D, and at \( T_0 > 320 \) K for T. Although the \( r_{diff} \) (600 s) increases rapidly with \( T_0 \), the monomers (H, D, and T) on the graphene should be diffusively immobile at any \( T_0 \) because the diffusion radius for each hydrogen-isotope monomer is very short at temperatures below the complete-desorption temperature above which there will be no residual monomer left for measurement. This type of diffusional immobility matches experimental measurements obtained on D monomers.3,18 The annealing process of D monomers on graphene at 298 K is visualized in
Figure 6b and c to compare with Hornekær et al.’s experiment in ref 3. In accordance with this experiment, the initial coverage (monomer number) is set to 0.03% \( n(0) \) \( \equiv 114 \) in a 100 nm \( \times \) 100 nm surface area (Figure 6b). After 10 min, only 33% of the monomers remain on graphene, a value that is comparable to the 20% observed in Hornekær’s experiment. The visualization of the annealing process in a for D monomers at room temperature (298 K) for 10 min. The area of the graphene surface is 100 nm \( \times \) 100 nm, and the initial coverage is set to 0.03% \( n(0) = 114 \) according to the experiment in ref 3.

Figure 5. Variation of the (a) desorption frequencies \( (V_{\text{des}}) \) and (b) diffusion frequencies \( (V_{\text{diff}}) \) of hydrogen-isotope monomers from the quantum mechanically modified hTST with respect to the inverse of temperature.

Figure 6. (a) Variation of the diffusion radius and the relative residual monomer number with respect to the annelling temperature \( (t_0 = 600 \text{ s}) \). The three gray dashed vertical lines at the complete-desorption temperatures of H, D, and T monomers (294, 312, and 332 K, respectively) are intended as a visualization tool. (b, c) The visualization of the annealing process in a for D monomers at room temperature (298 K) for 10 min. The area of the graphene surface is 100 nm \( \times \) 100 nm, and the initial coverage is set to 0.03% \( n(0) = 114 \) according to the experiment in ref 3.

of hydrogen monomers, which is not considered in this simulation; the interlayer interaction makes the hydrogen monomers easier to escape from graphite surface in experiments. As mentioned in the Methodology section, the interlayer interaction in bilayer graphene will lower the potential barriers by about 8 meV. This is because the bilayer graphene is less flexible than the monolayer graphene, which makes the monolayer graphene more reactive to bond with the hydrogen monomer. If a correction of \(-8 \text{ meV}\) is considered in the desorption activation energy, \( n(t_0)/n(0) \) equals 20% at 299 K. Thus, the interlayer interaction just results in a temperature difference of a couple of Kelvins, which indicates its weak effect on the kinetic properties of the hydrogen monomer and supports the validity of the monolayer structural model used in this report.

In some experimental measurements of kinetic properties, the temperature is increased at a constant rate \( (\alpha) \). The kinetic properties of hydrogen monomers under this constant-rate heating condition were simulated by eqs 10 and 11 with \( \alpha \) as 1.0 K/s. From eq 11, the relative desorption rate \( \frac{n(t_0)}{n(0)} \text{ at } T \) (Figure 7a) is determined both by the desorption frequency \( V_{\text{des}}(T) \) and by the residual monomer number \( n(t_0) \). On heating, \( V_{\text{des}}(T) \) increases with temperature or elapsed time (Figure 5) and \( n(t) \) decreases (Figure 7b); thus, there will be a desorption peak for each hydrogen-isotope monomer in the desorption spectrum of \( R_{\text{des}} \). The desorption peak for the H monomer is at 316 K, the desorption peak for the D monomer is at 336 K, and the desorption peak for the T monomer is at 344 K. In the desorption spectra, an isotope effect can be seen that a hydrogen monomer of lower mass is desorbed from the surface more easily, which is the same as the isotope effect in the annealing process. The same as discussed in the previous paragraph, the weak interlayer interaction will only make the desorption spectra move to lower temperatures by about 2 K.

In addition, when the coverage of hydrogen atoms on graphene increases, hydrogen dimers will form and dominate on the surface. In the desorption spectra under constant-rate heating (1.0 K/s), there are two peaks at 445 (490) K and 560 (580) K for H (D) dimers, which is totally different from the desorption spectra of H (D) monomer in Figure 7. The kinetic properties of hydrogen dimers on graphene and the effect of dimer–dimer interaction have been investigated by us using nearly the same method, which will appear in a forthcoming paper. Generally, the isotope effects, the localization nature of the vibrations of hydrogen dimers, and the dependence of the
kinetic properties on the localized modes are the same as those of the hydrogen monomer. This means that the investigation on the kinetic properties of hydrogen monomer on graphene is instructive to other more complex situations.

IV. Conclusions

The kinetic properties of hydrogen-isotope (H, D, and T) monomers on graphene were simulated using a composite ab initio method consisting of density functional theory, density functional perturbation theory, and harmonic transition state theory. The simulations were based on the potential barriers calculated from DFT and on the phonon spectra calculated from DFPT, which were used together to analyze calculated vibrational zero-point energy corrections, exponential prefactors (quantum mechanically modified and classical-limit), jump frequencies, and simulated kinetic properties. The chemisorption state and the desorption saddle-point state both have a magnetic moment of 1.0 μB, while the diffusion saddle-point state is nonmagnetic. From the electronic DOS analysis, in the desorption process, the hybridization of the hydrogen monomer with graphene is reduced and the contribution of the H(1s) orbital to the total magnetic moment increases. In the diffusion process, when leaving from the chemisorption state to the diffusion saddle-point state, this hybridization also decreases; the transferred electrons from H to graphene become more and more itinerant; the total magnetic moment decreases from 1.0 μB down to 0.0 μB. The spectra of the localized vibrational modes of hydrogen are hydrogen-mass-dependent, which results in the isotope effects in the kinetic properties (prefactor, activation energy, jump frequency, desorption rate, and diffusion radius) of H, D, and T monomers. The zero-point energy correction decreases with increasing monomer mass and is larger for desorption than for diffusion. This results in the isotope effect that a hydrogen monomer of lower mass is desorbed and diffuses more easily (with lower activation energies) and in that the desorption frequency of each hydrogen-isotope monomer is larger than its diffusion frequency. In the simulated 10 min annealing of hydrogen-isotope monomers on graphene, the monomers are quite diffusionally immobile at temperatures lower than the complete-desorption temperature, and a large fraction (67%) of the D monomers on graphene will be desorbed at the annealing temperature of 298 K. These theoretical results are very close to those obtained by experimental observations of hydrogen adatoms on graphite surfaces. The thermal desorption spectra (α = 1.0 K/s) of the hydrogen-isotope monomers have also been simulated. The resulting desorption peak for H is at 316 K, for D is at 336 K, and for T is at 344 K. The precise simulation of the kinetic properties of the hydrogen-isotope monomers on graphene described in this report can help to further precise studies of more complex hydrogenation processes. The precise theoretical predictions for radioactive tritium adatoms are especially useful because it is dangerous to conduct experiments on them in conventional laboratories.

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Supporting Information Available: The variation of the desorption and diffusion barriers with respect to the supercell size. This material is available free of charge via the Internet at http://pubs.acs.org.

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