Dynamics Studies of Diglycine Scattering from Highly Oriented Pyrolytic Graphite

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The dynamics of neutral diglycine collision with highly oriented pyrolytic graphite (HOPG) were studied by molecular dynamics simulations using a reactive force field. The simulations were performed at an initial incident energy of 481.5 kJ/mol for four different initial incident polar angles of 0°, 20°, 45°, and 70°, and a surface temperature of 677 K. The angular, translational and internal energy, and residence time distributions of the scattered products were determined and analyzed. As a polyatomic molecule, diglycine has several low frequency vibrational modes and shows a rather strong attraction to HOPG, which leads to a long residence time on the surface and facile energy loss, particularly along the normal surface. Since there is significant normal momentum lost while parallel momentum is partially conserved, the scattering angular distribution is found to be generally superspecular and the final translational energies are much lower than the values predicted by the so-called hard-cube model. This study extends our knowledge of collisional energy transfer during collisions of polypeptide molecules with HOPG, which is expected to help the design of a neutral-gas concentrator for the fly-by collection of such molecules in rarefied atmospheres.

Key words: Surface, Scattering, Energy transfer

I. INTRODUCTION

There has recently been much interest in searching for life-signature organic molecules in tenuous planetary atmospheres using fly-by satellites. In such far-flung explorations, on-board mass spectrometry is often used to identify these molecules of interest [1, 2]. However, low-concentrations of such neutral molecules in rarefied atmospheres pose a serious challenge. One possible solution is a gas concentrator, which has a funnel like inlet that couples to a collection chamber, designed to mitigate the low number density of such molecules [3]. Scattering of molecules from specially designed concentrator walls leads to the accumulation in the collection chamber. The design of such a neutral-gas concentrator requires knowledge of scattering behaviors of relevant molecules, which is the primary motivation of the current work. In particular, we focus here on the scattering of a dipeptide molecule (diglycine) from highly oriented pyrolytic graphite (HOPG) surfaces.

HOPG consists of stacked graphene sheets held together by weak van der Waals interactions. These sheets are rather stable and inert. In addition, its two-dimensional honeycomb lattice is relatively flat due to the sp² hybridization of the constituent carbon, which is expected to lead to relatively simple scattering dynamics. As a result, it has been considered as an ideal material for the neutral-gas concentrator. There have been many scattering studies on HOPG, including both atoms (Ar [4] and Xe [5]) and small molecules (O₂ [6–8], N₂ [9–11], CO₂ [12], and H₂O [12]). These studies suggest that scattering of such projectiles from HOPG can often be quite satisfactorily described by a simple hard-cube model (HCM) [13, 14], which assumes parallel momentum conservation. In addition, the trajectories of scattered molecules were found to fall into three main types as single collision, multiple collisions with escape, and trapping without escape [10–12]. For most of such species, trapping only represents a small portion of the scattering.

The scattering dynamics of larger polyatomic molecules are more complicated than those of atoms and small molecules, since the incident kinetic energy can be transferred into the ro-vibrational modes of molecules, as well as the surface motions [15]. As already shown in our previous study, the scattering of the glycine molecule from HOPG has rather different dynamic behaviors from those of H₂O and CO₂ [12]. The stronger molecule-surface interaction leads to more energy transfer and a longer residence time during glycine...
scattering. Indeed, the energy loss significantly deviates from the HCM prediction. What is more, large organic molecules may also dissociatively scatter if too much energy is transferred to internal modes during an impulsive collision, in which one or more weak bonds may be broken, leading to the so-called “shattering” [16]. These behaviors are expected to significantly impact on the efficiency of the concentrator in collecting such molecules.

In this work, we explored the scattering dynamics of neutral diglycine from an HOPG surface. Diglycine can be obtained from the condensation reaction of two glycine molecules forming a peptide bond, which represents a simple model for understanding the scattering of other peptides and more complex biomolecules. Experimentally, it is difficult to vaporize the dipeptide molecule for technical reasons, thus theoretical simulations are vital for us to understand the scattering dynamics. Here, we report detailed molecular dynamic simulations using a reactive force field to understand the scattering dynamics and energy transfer efficacy.

II. SIMULATION DETAILS

Empirical reactive force fields (ReaxFFs) [17, 18] have been successfully applied for many gas-surface processes, including hyperthermal oxygen interaction with silicon surfaces [19], O2 sticking on the Pt(111) surface [20], and CO collision with an O-preadsorbed silica surface [21]. Since ReaxFF has high computational efficiency, it enables long-time simulations with small statistical errors. We have also recently used the same strategy in studying scattering of some small molecules (CO2 and H2O) and glycine from HOPG surfaces and successfully reproduced experimental observations [12]. In this work, the ReaxFF parameters for diglycine were obtained from the work of Rahaman et al. [22], which have been successfully applied to study diglycine/TiO2 surface interactions [23]. The ReaxFF parameters for graphene were adapted from previous studies [24, 25]. For the diglycine and graphene interaction, only van der Waals terms are included and the corresponding parameters for each single atom type are obtained from previous simulations of van Duin et al. [25, 26], which have been used to study the scattering dynamics of N2/graphene [11], CO2/graphene [12], H2O/graphene [12], and glycine/graphene [12] with the results in good agreement with experiment.

In our model, the graphite(0001) surface consists of six carbon layers with (8×8) surface cells that contain 128 carbon atoms per layer, with periodic boundary conditions. Molecular dynamics simulations were performed using the large-scale atomic/molecular massively parallel simulator (LAMMPS) software [27]. The surface temperature (Ts=677 K), which was the experimental temperature [12], was simulated by initiating the surface with a Maxwell-Boltzmann distribution for surface atomic positions and velocities with the bottom layer fixed, followed by 20 ps equilibration with an isobaric-isothermal (NPT) ensemble with the periodic cell held at a constant pressure of 1 atm using a Berendsen barostat with a damping constant of 50 fs and a Berendsen thermostat with a coupling of 10 fs. This was followed by an extra 30 ps microcanonical (NVE) simulation. 1000 snapshots of the slab in the last 10 ps of the NVE simulations were saved every 10 fs, which served as the initial configurations of the thermalized slab in the corresponding scattering simulations.

As shown in FIG. 1, the neutral diglycine (C4H9N2O3) molecule has several functional groups with a large number of conformations due to many single bond rotamers. It has been reported that diglycine contains 28 different cis and trans conformers, within a small energy range of 0–12.5 kcal/mol [28]. In order to sample those plausible structures, an NVT simulation of the isolated molecule was performed for 4 ps with a time step of 0.1 fs at the temperature of 300 K, which enabled the diglycine molecule to sample different conformers. 1000 structures with corresponding momenta of the final 1 ps of the simulation were saved for the initial condition of the molecule in the scattering simulations.

The trajectories were initiated with the gas molecule located far above the surface (Z=17.0 Å), where the interaction energy between the molecule and surface is zero. The incident kinetic energy was set to 481.5 kJ/mol, which gives roughly the same speed as the other molecules studied in supersonic experiments [12]. The initial lateral coordinates of the diglycine molecule were randomly chosen in the surface unit cell. The initial incidence polar angle was set to both normal and off-normal directions (θi=0°, 20°, 45°, and 70°), with the azimuthal angle sampled randomly in the [0°, 360°] range. The timestepes were set to 0.1 fs. 1000 trajectories were run for each set of initial conditions.

The trajectories were terminated after the molecule scattered back beyond 17.1 Å above the surface or after a maximum propagation time of 50 ps. For molecules scattered from the surface, the final translational energy ET, polar angle (θt, with respect to the surface normal), and the change in azimuthal angle, Δφ, were evaluated. The rotational and vibrational energies of the scattered molecule were also determined approximately by neglecting the rotation-vibration coupling. To this

FIG. 1 Structure of diglycine.

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end, the Cartesian coordinates $\vec{r}_i$ and momenta $\vec{p}_i$ of all atoms in the scattered molecule were obtained in the center-of-mass (COM) frame directly from the classical trajectories. The angular velocity $\vec{\omega}$ of the molecule was calculated by $\vec{\omega} = I^{-1} \vec{L}$, where $I$ is the moment of inertia tensor and $\vec{L} = \sum \vec{r}_i \times \vec{p}_i$ is the angular momentum for the molecule. The vibrational energy consists of kinetic and potential energies. The former was determined by the vibrational velocities $\vec{v}'_i = \vec{v}_i - \vec{\omega} \times \vec{r}_i$ after the COM velocities were removed, while the latter was from the ReaxFF force field of the molecule.

To analyze the trajectories, we determined the number of inner turning points (ITPs) [8, 10–12] in the collision, defined as the point where sign of the normal momentum of the molecular COM changes from last point. Three trajectory types were identified: impulsive scattering (IS with one ITP), extended impulsive scattering (EIS with more than one ITP), and trapping (T, still on the surface at the maximum simulation time). It should be noted that the T trajectories might eventually desorb thermally at a time longer than the 50 ps simulation time.

III. RESULTS

FIG. 2 shows the interaction potential between diglycine and a single-layer graphene for six typical molecular configurations. G1–G3 are the trans structures and G4–G6 are the cis ones, which are two possible conformations for diglycine [28]. G1 and G2 are the two most stable structures in the gas phase. The strongest interaction with the graphene ($-68.8$ kJ/mol) is for the G2 structure, which orients parallel with the surface with a COM coordinate of $Z=3.2$ Å. On the other hand, the G1 structure has the weakest adsorption of $-47.8$ kJ/mol at $Z=4.0$ Å with the NH2 group directed toward, and the COOH group pointing away from the surface. G2–G6 are the intermediate cases in terms of adsorption energy. The adsorption energies are much larger than that of glycine ($-37.6$ kJ/mol) [12]. This is partly because diglycine has more atoms, which results in stronger interaction. It also has more possible conformations, enabling interactions with the surface via different functional groups and different rotamers. These potential energy curves already suggest more complex scattering dynamics than simpler molecules.

The percentage of different scattering types and their dependence on the incident angle $\theta_i$ are shown in Table I. As $\theta_i$ increases, as expected, the percentage of IS decreases, while those for EIS and T increase. The dependence on $\theta_i$ is quite similar to that of N2, CO2, H2O and glycine scattering from HOPG [10, 12], which is linked to the extent of normal dissipation of the incident energy $E_i$ during the collision with the surface. However, diglycine scattering has significantly less direct scattering than small molecules such as H2O and CO2. According to our previous work, H2O (CO2) scattering from HOPG has IS probabilities of 68.4% (79.6%) and 45.3% (45.5%) at $\theta_i=45^\circ$ and $70^\circ$, respectively [12], in contrast to 39.2%, and 14.9 % for diglycine.

On the other hand, diglycine has much larger trapping probabilities, 23.1% and 46.2% at $\theta_i=45^\circ$ and $70^\circ$, respectively, much larger than those of glycine, 9.0% and 14.3% [12]. In contrast, H2O has no trapping events and CO2 has small trapping probabilities less than 2% at $\theta_i=30^\circ$, 45°, and 70° [12]. The larger trapping probabil-

<table>
<thead>
<tr>
<th>$\theta_i$/$^\circ$</th>
<th>IS</th>
<th>EIS</th>
<th>T</th>
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<tr>
<td>0</td>
<td>59.8</td>
<td>28.4</td>
<td>11.8</td>
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<td>20</td>
<td>56.7</td>
<td>30.6</td>
<td>12.7</td>
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<td>45</td>
<td>39.2</td>
<td>37.7</td>
<td>23.1</td>
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<td>70</td>
<td>14.9</td>
<td>38.9</td>
<td>46.2</td>
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FIG. 2 ReaxFF interaction energies of diglycine with graphene as a function of the molecule-graphene distance for six different glycine configurations.
FIG. 3 Translational, rotational, vibrational, and total energy distributions for the scattered molecule at θi=0° (a), 20° (b), 45° (c), and 70° (d). The gray dashed lines denote the incident energy of the impinging molecule.

TABLE II Calculated average translational and internal energies (E_T and E_int in kJ/mol) of the scattered molecules, and average energy exchange for different scattering mechanisms. The values in the parentheses are percentages of the incident energy.

<table>
<thead>
<tr>
<th>θi/(°)</th>
<th>IS</th>
<th>E_T</th>
<th>E_int</th>
<th>E_ex</th>
<th>E_T</th>
<th>E_int</th>
<th>E_ex</th>
<th>E_T</th>
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<th>E_ex</th>
<th>Total</th>
<th>E_int</th>
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<tr>
<td>0</td>
<td></td>
<td>46.5</td>
<td>237.2</td>
<td>197.8</td>
<td>15.3</td>
<td>234.2</td>
<td>231.9</td>
<td>36.5</td>
<td>236.2</td>
<td>208.8</td>
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<td>(9.7%)</td>
<td>(49.3%)</td>
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<td>20</td>
<td></td>
<td>88.6</td>
<td>225.7</td>
<td>167.2</td>
<td>44.9</td>
<td>233.6</td>
<td>202.4</td>
<td>73.3</td>
<td>228.6</td>
<td>179.6</td>
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<td>(18.4%)</td>
<td>(46.9%)</td>
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<td>45</td>
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<td>228.3</td>
<td>189.8</td>
<td>63.4</td>
<td>151.5</td>
<td>220.4</td>
<td>109.6</td>
<td>190.5</td>
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<td>70</td>
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<td>401.5</td>
<td>149.6</td>
<td>−69.6</td>
<td>246.0</td>
<td>215.2</td>
<td>20.3</td>
<td>289.0</td>
<td>196.2</td>
<td>−3.7</td>
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<td>(83.4%)</td>
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<td></td>
<td>(60.0%)</td>
<td>(40.8%)</td>
<td>(−0.8%)</td>
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The calculated translational, rotational, vibrational, and total energy distributions of the scattered molecules are displayed in FIG. 3 for different θi. The average translational energy (E_T), internal energy (E_int) of the scattered molecules, and average energy exchange (E_ex) between the molecule and surface are shown in Table II for both the IS and EIS types. E_ex is defined as the initial total energy (sum of the incident and internal energies) of the impinging diglycine subtracting the total energy of the scattering molecule. A positive or negative value of E_ex indicates that the molecules lose energy to, or gain energy from the surface. The internal energy is defined as the sum of the rotational and vibrational energies of the molecule.

For all cases in FIG. 3, the rotation is only slightly excited within several tens of cm⁻¹, due to the rather flat HOPG surface which exerts weak torque forces on the impinging molecule. Similar to the glycine scattering [12], E_T increases rapidly with the increasing θi, while the E_int slowly decreases. On the other hand, E_T for EIS is much lower than the corresponding value for IS, which can be attributed to more efficient energy dissipation into both the surface and internal modes of the molecule. E_int values for IS and EIS are almost identi-
especially for larger incident angles, indicating the dom-

tering plane. The distributions of $\Delta \phi$ azimuthal angle change with respect to the incident scat-

tering are shown in FIG. 5. Here $\Delta \phi$ are listed in Table IV and the distributions of which

of the azimuthal angle and glycine from HOPG [12].

scattering of methyl formate [30], nitromethane [30],

the predictions of the HCM were also observed for the

below the HCM prediction. Significant deviations from

$\theta$ exceeding the incident energy when

$\theta$ entering molecule increases with increasing

tained in IS scattering. The total energy of the scat-

tering molecule changes with increasing $\theta_i$, and some

exceed the incident energy when $\theta_i=45^\circ$ and 70$^\circ$. As

shown in Table II, the impinging molecules mostly lose energy to the surface at the low incident angles, while

the impulsive scattered, so the total scattered molecules with $\theta_i=70^\circ$ have negative $E_{\text{cs}}$ values as it gains energy from the surface. As has been reported for glycine scattering [12], these molecules tumble along the surface for a long time before desorbing back to the vacuum, which leads to more energy transferred through the successive molecule-surface interactions.

Table III shows the average normal and parallel translational energies ($\langle E_{\perp} \rangle$ and $\langle E_{\parallel} \rangle$). Both normal and parallel momenta participate in energy transfer. In all cases, however, only a small fraction (within 10%) of the normal energy is retained, while more than 20% of initial parallel energy remains, depending on $\theta_i$. The loss of parallel momentum indicates molecules do suffer from corrugation on the surface. The much larger normal momentum loss implies that normal momentum is accommodated more efficiently than the corresponding parallel one, which gives rise to the superspecular scattering. The $E_T/E_i$ ratios and HCM prediction, namely $E_T/E_i = \sin^2 \theta_i / \sin^2 \theta_i$ [29], are compared in FIG. 4 as a function of $\theta_i$. The dependence of $E_T/E_i$ on $\theta_i$ falls below the HCM prediction. Significant deviations from the predictions of the HCM were also observed for the scattering of methyl formate [30], nitromethane [30], and glycine from HOPG [12].

The averaged polar angles $\langle \theta_i \rangle$ and averaged changes of the azimuthal angle ($\Delta \phi$) for the scattered molecules are listed in Table IV and the distributions of which are shown in FIG. 5. Here $\Delta \phi = |\phi_i - \phi_i|$ is the final azimuthal angle change with respect to the incident scattering plane. The distributions of $\Delta \phi$ is quite narrow, especially for larger incident angles, indicating the dom-

inance of in-plane scattering. This is another manifestation of the weakly corrugated HOPG surface. All $\langle \theta_i \rangle$ have a value larger than the specular angle as $\langle \theta_i \rangle > \theta_{\text{spec}}$, due to the efficient accommodation of the normal momentum whilst the parallel momentum is retained to some degree.

The distribution of the surface residence time for EIS cases is presented in FIG. 6. The residence time is the time required for a trajectory to enter and exit the scattering zone, which is defined by a vertical distance of 6.0 Å between the molecular COM and the surface plane (the topmost graphene layer). For IS, the scattering is fast and the residence time is only a few hundred fs. On the other hand, EIS trajectories take a much longer time to escape from the surface. The averaged residence time for incident angle $\theta_i$ of 0$^\circ$, 20$^\circ$, 45$^\circ$, and
FIG. 5 Probability of scattering angle $\theta_f$ (left panel) and change in the azimuthal angle, $\Delta \phi_f$ (right panel) for scattering molecules at $\theta_i=0^\circ$ (a, e), $20^\circ$ (b, f), $45^\circ$ (c, g), and $70^\circ$ (d, h).

FIG. 6 Distributions of residence time for EIS scattering molecule with $\theta_i=0^\circ$ (black bars), $20^\circ$ (blue bars), $45^\circ$ (cyan bars), and $70^\circ$ (red bars).

$70^\circ$ are 9.0, 10.5, 11.3, and 14.5 ps, respectively. As discussed above, the impinging molecules at large incident angles have smaller normal momenta and easily undergo multiple collisions. On the other hand, the molecules have more parallel momentum at the large incident angle, most of which are retained after scattering as shown in Table III. The incident energy loss and the width of scattering angle distribution as a functional of incident angle decrease, while the residence time increases.

IV. CONCLUSION

The scattering dynamics of a dipeptide molecule, diglycine, from the HOPG surface has been investigated theoretically using classical molecular dynamics based on a ReaxFF reactive force field. The diglycine has a large adsorption energy and many low frequency vibrational modes, which influence the diglycine-HOPG scattering. The scattering of diglycine at the incident energy of 481.5 kJ/mol leads to different trajectory types. Direct impulsive scattering dominates at low incident angles of $0^\circ$ and $20^\circ$, but decreases with increasing $\theta_i$, while extended impulsive scattering and trapping show opposite trends. Compared to small molecules such as H$_2$O and CO$_2$, diglycine has a much lower percentage of direct scattering. This is due to the fact that diglycine interacts with the surface much more strongly, and that it has more energy dissipation channels. No surface-induced dissociation event was observed.

For all cases, the rotational excitation in the scattered molecule is quite small, due to the relatively flat surface. On the other hand, diglycine can easily transfer initial translational energy into either the surface or some internal degrees of freedom of the molecules. Both impulsive scattering and extended impulsive scattering show high internal excitation, suggesting facile direct translation-to-vibration energy transfer, even when there is only a single collision. This is especially true at low incident angles, where the larger normal component of the incident energy leads to higher internal energy excitation. The scattered diglycine mainly undergoes in-plane scattering and the scattering angles have a superspecular angular distribution, as the normal momentum loss is more effective while parallel momentum can be partially conserved. As a result, the $(E_f)/(E_i)$ ratio along the scattering angle falls below the values predicted by the hard-cube model, similar to the case of glycine scattering from HOPG. The residence time of diglycine on the HOPG surface increases with the incident angle, and the distribution has a long tail extending to 45 ps.

This study contributes to a better understanding of the scattering dynamics of diglycine from the HOPG surface.
of scattering dynamics of floppy polyatomic molecules from the HOPG surface, which sheds light on designing and modeling an effective and efficient neutral-gas concentrator for large life-signature molecules such as amino acids and polypeptides. The much more efficient energy loss in diglycine scattering from HOPG suggests that the quasi-elastic scattering observed for small and rigid molecules is much less likely for larger and floppy molecules. This important observation needs to be carefully considered when designing the gas concentrator.

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