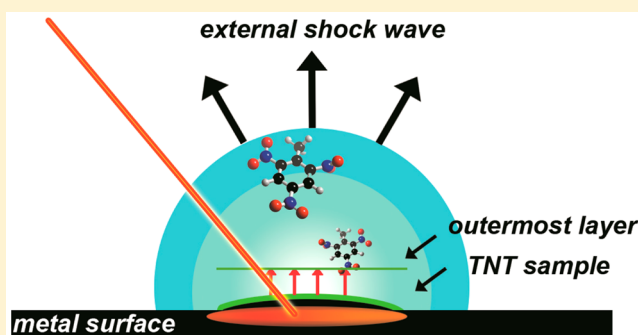


Mechanism of Intact Adsorbed Molecules Ejection Using High Intensity Laser Pulses

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S Supporting Information

ABSTRACT: A novel universal mechanism for the ejection of intact, neutral molecules from thin films into the gas phase initiated by high intensity ultrashort laser pulses is described. The proposed mechanism is substantiated by detailed reactive molecular dynamics simulations. In the present study, 2,4,6-trinitrotoluene (TNT) and cryogenic benzene are used as thin film targets. According to the proposed mechanism, the laser pulse, absorbed by the substrate, forms a hot plasma plume which in turn generates a shock wave that moves across the deposited thin film. The simulations indicate that the shock wave propagates through the thin film without dissipation and eventually ejects molecules from the free surface. It is revealed that the proposed mechanism is feasible only in a limited range of shock velocities. The results compare well qualitatively with recent experimental findings of femtosecond, nonresonant, laser-induced desorption. Simple experimental measurements are outlined to validate the proposed mechanism.



INTRODUCTION

A recently developed laser-based mass spectrometric technique, termed as laser electrospray mass spectrometry, LEMS,¹ has become a simple universal method to sample solid materials at ambient conditions using mass spectrometry. In a typical experiment, a sample is placed on top of a solid surface (as a thin film) and then exposed to intense, ultrashort, nonresonant laser pulses for subsequent single molecule vaporization and mass-spectral analysis. The process does not necessitate the use of a matrix, unlike in other methods of laser assisted desorption/ionization (MALDI).² Surprisingly, LEMS generates intact molecules ejection with negligible chemical decomposition of the material being analyzed. The method has been used to transfer a wide variety of nonvolatile polyatomic molecules from the solid phase into the gas phase. Studied systems range in molecular sizes from benzene and organic explosives (RDX, TATP, HMTD), up to proteins and plant tissue.^{3–5} Initial experimental studies^{6–8} concentrated on desorption of mono- and multilayer benzene films deposited on Pt[111] irradiated by 800 nm pulses of 150 fs and 200 ps duration. Several attempts in recent years have been made to decipher the underlying mechanism. It was shown that both purely thermal (phonon mediated) and electronic (single or multiphoton) mechanisms can be disregarded based upon the following observations: (a) In the case of the benzene/Pt[111] system, even at 1 ML coverage, a bimodal nonthermal distribution of

velocities was observed. (b) Saturated hydrocarbons, that have zero first-, second-, or third-order absorption cross sections for the 800 nm wavelength, should show substantially lower desorption yields than aromatic species. However, this was found to be untrue, excluding the direct molecular excitation mechanism.^{7,8} (c) Desorption induced by multiple electronic excitations seemed equally improbable due to the extremely small cross sections of multiphoton absorption. Moreover, maximum yield of desorption was obtained with intermediate 10–20 ps pulse widths, instead of the quick “switch-off” expected for longer duration pulses.⁷

While the above mechanisms were regarded as equally improbable, the underlying mechanism remains elusive. In this study, a novel mechanism based on the theory of laser-matter (metal/dielectric) interactions is proposed.⁹ Below, we briefly review the physical principles of the process and then outline the simulations protocol.

In a typical LEMS experiment, laser intensity is kept near, or slightly above, the ablation threshold of the substrate material and pulse duration is ultrashort (fs range). Common laser parameters that were used for desorption of organic explosives (RDX, TATP and HMTD) are $I \sim 10^{13}$ W/cm²; $\tau = 70$ fs and $\lambda = 800$ nm.⁴ These parameters result in an energy density of

Received: April 12, 2016

Revised: April 22, 2016

Published: April 26, 2016

$\sim 0.7 \text{ J/cm}^2$, which is slightly above the ablation threshold of stainless steel ($0.13\text{--}0.16 \text{ J/cm}^2$) used as a substrate.^{10,11} At these conditions, no laser–plasma interaction is operable, so the full laser energy can be efficiently deposited into the target with minimal collateral damage.¹² Shorter pulses require higher laser intensities ($10^{13}\text{--}10^{14} \text{ W/cm}^2$) compared to longer pulses. At these intensities, practically any substrate (metal or dielectric) will begin to ionize early during the laser pulse.⁹ Consequently, the interaction of both metals and dielectrics with an ultrashort laser proceeds in a similar fashion. A key phenomena bridging LEMS experiments and our proposed mechanism lies in the ablation stage of the substrate material.

Ablation is the generation and ejection of material plume in a state of high-temperature and pressure plasma. This process starts at early stage of every laser pulse and continues up to several hundred nanoseconds later. The laser generated plasma plume propagates outward normal to the surface at supersonic velocities, thus acting much like a mechanical piston colliding with the deposited film. Its expansion dynamics under vacuum conditions can be described by the self-similar model of Anisimov et al.¹³ and the simple point blast model.¹⁴ In the presence of a background gas (or a thin film as in the present case), Anisimov's equations become more complex. The plume compresses the surrounding gas or thin film, and a primary shock wave is generated that soon decouples from the plume-gas contact surface.^{15,16} Thus, we model the plasma plume impact on the thin film using a mechanical piston, with a predetermined impact velocity shot toward a TNT thin film, chosen to represent a template organic solid (Figure 1). We

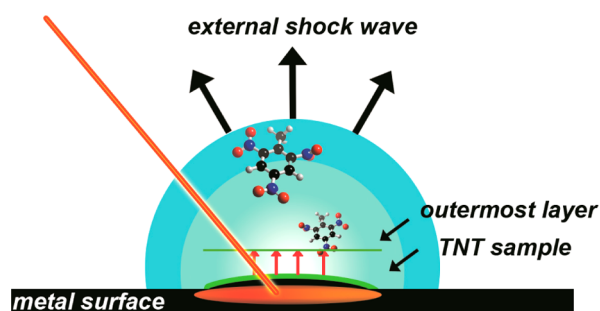


Figure 1. Interaction of an intense, nonresonant, ultrashort laser pulse with a metal surface generates an outward propagating shockwave. A solid TNT sample, transparent to the laser, experiences a mechanical impact on a femtosecond time scale due to a plasma plume formation and supersonic expansion.

observe the generation of shock waves with different propagation velocities depending on the piston impact velocity. For the appropriate conditions, single molecules and clusters are ejected from the free surface. The cluster size distributions, translational velocities, temperatures, and further decomposition processes are analyzed and related to the initial conditions.

COMPUTATIONAL DETAILS

Molecular dynamics (MD) simulations were conducted using the LAMMPS open-source package.¹⁷ The simulations used the ReaxFF force field suited for nitramine and nitroaromatic energetic materials. This force field was validated in the past to be accurate for the description of gas phase and condensed phase TNT.^{18,19} A starting geometrical configuration was generated using the experimental unit cell obtained from the Cambridge Structural Database (database code: CSD

ZZZMUC01) and subsequently multiplied in the (a,b,c) lattice directions to obtain a $10 \times 6 \times 2$ super cell with dimensions: $149.9 \times 36.2 \times 39.36 \text{ \AA}^3$. The system was energy minimized with the conjugate gradient method before a thermalization stage in which a Berendsen thermostat at 50 K was used for 30 ps with coupling constant of 25 fs. A piston was created by separating the left 6 ML of TNT by 20 Å to the left (see Figure S1 in the Supporting Information). Nonequilibrium simulations of impact used a time step of 0.1 fs and lasted up to a few ns in duration depending on piston impact velocity. During the simulation, bond formation and rupture events were monitored every time step and properly averaged over 10 steps that are 10 fs apart. This procedure overcomes the possibility of false bonds identification during possible short-lived high energy encounters. Each possible atomic pair was assigned a different bond order cutoff value to properly identify chemical species (standard values for C/H/O/N high-energy simulations). Thus, each pair having a higher cutoff than the specified value is considered to be covalently bonded.

RESULTS

I. Laser–Substrate Interaction and Impact. Several experimental studies have reported velocity distributions of ejected particles under the action of ultrashort pulses. For example, time-resolved measurements of plasma evolution with ultrashort, 200 fs, 20 J/cm^2 laser pulses on C75 steel in ambient air have identified two regimes of material ejection.²⁰ In the first 30 ns, a linear regime was obtained, similar to vacuum conditions, where velocities of $\sim 4 \text{ km/s}$ were recorded. At later time, a second, slower regime with $\sim t^{2/5}$ time dependence of the expansion front was found. Further studies of laser ablation of copper and silicon surfaces with ultrashort low and moderate intensity laser pulses have measured ejection velocities of neutral particles and molecular fragments with corresponding shock wave velocities in the range 4–8 km/s.^{21–23}

It is possible to estimate the expanding plume velocity suitable for the case of LEMS experiment using a combination of the linear model (suitable to describe the dynamics during the initial few tens of ns) and the point blast wave model for longer propagation times. This description was verified in an experimental study of ultrashort laser irradiation of stainless steel targets.²⁰ Using considerations of energy conservation and similarity arguments, it was shown²⁴ that early plume propagation in the case of fs pulses under both vacuum and ambient gas atmosphere is adiabatic and follows free expansion dynamics. At longer propagation times, the expansion resembles a strong point explosion where a homogeneous medium is assumed and energy is released instantaneously. The dynamics in each regime can be approximately determined by the following simple equations relating the plume front position to material and laser parameters:

Linear model:

$$R(t) \approx \left(\frac{E_0}{\xi_g M_v} \right)^{1/2} t \quad \text{for } t < \sim 10^1 \text{ ns}$$

Point Blast Wave model:

$$R(t) \approx \xi_{sw} \left(\frac{E_0}{\rho g} \right)^{1/5} t^{2/5} \quad \text{for } R_s > t > \sim 10^1 \text{ ns}$$

where $R(t)$ is the position of the plume front, E_0 is the effective laser energy absorbed by the shock wave, ρ_g is density of ambient gas, M_v is the mass of plume, ξ_{sw} and ζ_g are coefficients depending on gas and symmetry (i.e., spherical expansion), respectively, and R_s is the transition time to the Sedov regime where plume mass becomes similar to the displaced medium mass.²⁴ Using characteristic values for stainless steel in air under ultrashort laser pulses⁴ and assuming $E_0 = 1\%$ of laser pulse energy ($M_v = 10$ ng, $\rho_g = 1.18$ kg/m³, $E_0 = 0.05$ mJ) with typical²⁰ values of $\xi_{sw} \approx 1$ and $\zeta_g \approx 3/20$, one obtains a plume propagation profile shown in Figure 2. The profiles of the

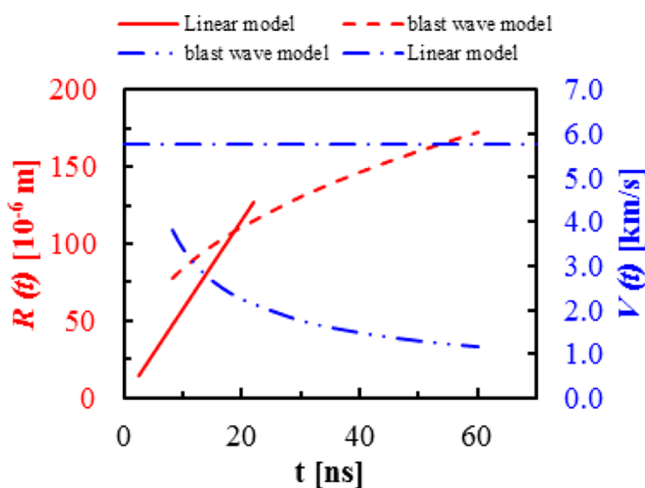


Figure 2. Plasma plume position and propagation velocity following ultrashort laser pulse on steel surface. Early propagation can be described by the linear model similarly to experiments in vacuum,²⁰ while at later times the presence of the surrounding gas is more evident following a $R \sim t^{2/3}$ time dependence.

plasma plume front position, $R(t)$, and its corresponding velocities, $V(t)$, as obtained from the time derivative of $R(t)$, are shown in Figure 2 as a function of time up to 70 ns following an ultrashort laser pulse irradiation. In the early stages of plume motion, the propagation of the plume is fastest with a characteristic velocity of nearly 6 km/s. This value is independent of surrounding gas and is located in the free expansion (vacuum) regime. A few nanoseconds later, deceleration is evident to lower velocities due to the growing effect of the surrounding media (gas or deposited material).

II. ReaxFF Simulations of Impact. In order to verify whether supersonic plasma plume impacts can indeed lead to the ejection of intact organic molecules, ReaxFF simulations^{18,19} of a piston impact on a thin film of TNT were conducted. The choice of TNT as the target material strengthens the potential validity of the results due to its relatively high reactivity and ease of decomposition compared to inert aromatic materials. The computational model consists of two moieties: a piston and a target and is shown in Figure S1 in the Supporting Information. The piston was given an initial velocity in the longitudinal direction ranging from 2 up to 7 km/s in addition to its thermal energy. These impact velocities are characteristic of expanding plumes following ultrashort laser ablation of metal surfaces, as was found above.

Analysis of mild impacts ($v_{\text{imp}} = 2\text{--}3$ km/s) revealed that the resultant shock waves propagate through the thin film with velocities of $v_{\text{shock}} = 5\text{--}6$ km/s. These systems showed no chemical decomposition whatsoever, apart from incomplete intermolecular bond dissociation (overcoming van der Waals interactions) and the formation of various size clusters (Figure 3). The clusters formed following the impact further disintegrate, so by the end of simulation time ($t_{\text{end}} = 100$ ps) six smaller clusters were obtained with an average size of 96 molecules per cluster. The disintegration process into clusters is the result of partitioning the initial impulsive energy between fragmentation of the layer into clusters, kinetic energy of the moving clusters and their internal (vibrations, bending motion, etc.) energies during the material ejection from the substrate. Further tests were conducted to check dependence on simulation duration to examine whether longer simulation times are required to obtain complete disintegration into isolated molecules. Three typical clusters with different sizes (small, ~ 30 molecules; intermediate, ~ 50 molecules; and large, ~ 100 molecules) were extracted at $t_{\text{end}} = 100$ ps from the system initiated by a 3 km/s piston. These clusters were allowed to continue their time evolution for up to 2 ns, a 20-fold longer. We found that the clusters continued to disintegrate, transferring energy from translation into internal degrees of freedom of the cluster. At the end of 2 ns, single TNT molecules and transient vdW-type dimers were the only species observed. In the case of 2 km/s impacts, the target disintegrated into two large clusters that remained stable (no further disintegration into smaller clusters occurred) during 2 ns time scale.

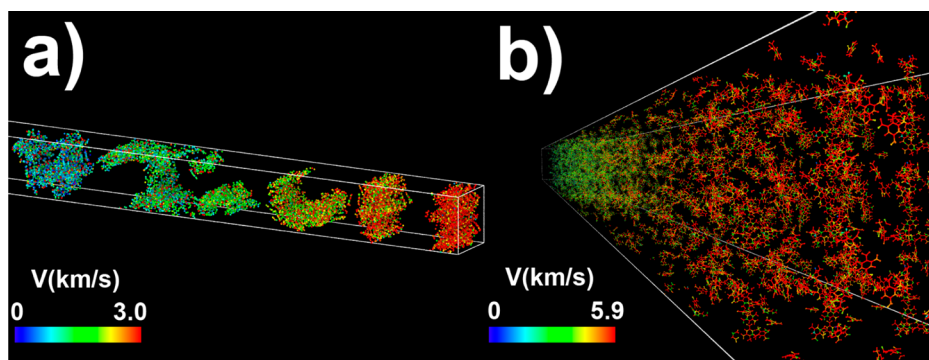


Figure 3. Ejection of species following impact velocities of (a) $v_{\text{imp}} = 3$ km/s and (b) $v_{\text{imp}} = 6$ km/s. Impact velocities $6 \text{ km/s} \geq v_{\text{imp}} \geq 3 \text{ km/s}$ result in small clusters and isolated molecules ejection with negligible chemical decomposition ($<10\%$), while velocities $v_{\text{imp}} < 3 \text{ km/s}$ lead to the ejection of stable intermolecular (vdW type) clusters. Colors indicate a molecule center-of-mass velocity scale bar (units: km/s).

Using higher piston impact velocities (5–6 km/s) leads to size distribution of the ejected material that is almost immediately centered on single molecules, with minor amounts of van der Waals bound dimers, trimers as well as very small amount of additional molecular decomposition products. The calculated shock wave velocity across the TNT film following a piston impact of $v_{\text{imp}} = 6$ km/s is $v_{\text{shock}} = 9$ km/s. This shock wave is traversing the multilayer in a mere 1 ps and leads to the ejection of mostly intact molecules into the gas phase (vacuum in the simulations here). At 6 km/s impact, $\sim 93\%$ of the initial TNT molecules remained intact with negligible amount of the vdW dimers, while the remaining $\sim 7\%$ undergo decomposition into a variety of transient intermediates and stable gaseous products. Careful analysis of the decomposition products identity (Figure 4) shows that they contain covalently bound

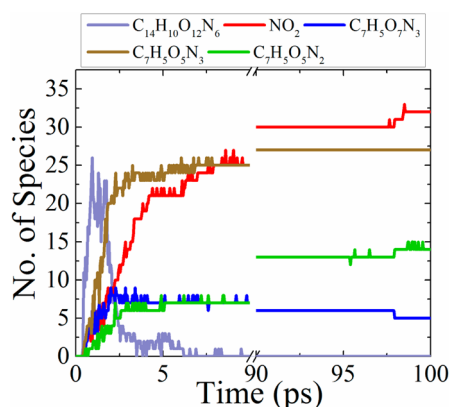


Figure 4. Main decomposition products obtained following a 6 km/s impact on a TNT multilayer. To properly identify chemical species and prevent artificial short-lived chemical bonds, an averaging procedure of bond orders was performed.²⁵

fragments of TNT dimers with the elemental composition $C_{14}H_{12}O_{10}N_6$ that appear immediately after impact (~ 1 ps); they reach a peak value approximately 2 ps following the impact and then sharply decrease to negligible amounts. The disappearance of these intermediates is due to their decomposition into smaller radical fragments such as $\cdot C_7H_5O_3N_3$, $\cdot C_7H_5O_3N_2$, $\cdot C_7H_5O_7N_3$, and $\cdot NO_2$. The amount of different final fragments reach a constant value of approximately 30 species that remains constant until the end of the simulation (100 ps).

Impact velocities lower than 6 km/s result in no chemical decomposition whatsoever. Impact velocities above 6 km/s, lead to a much higher percentage (40–100%) of decomposition. Thus, it seems that there exists a window of piston impact velocities to obtain intact molecules ejection that resides roughly in the range of $v_{\text{imp}} = 3$ –6 km/s.

The center-of-mass velocity distributions of the ejected molecules for the case of 6 km/s impact are shown in Figure 5. At the beginning of the simulation, ~ 750 fs after the piston impacts the target molecular multilayer, molecules at the impacted surface (metal–multilayer interface) acquire high velocities (average value ~ 3 km/s). The momentum acquired by the molecular layer at the substrate–adsorbate interface, due to the initial impulse, propagates across the molecular multilayer almost without dissipation with nearly constant velocity. This momentum transfer across the molecular layer resembles soliton like propagation.²⁶ Once the soliton like wave reaches the molecular layer edge, part of it is reflected back

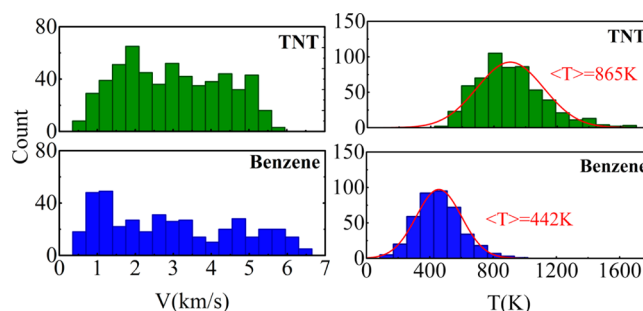


Figure 5. Center of mass velocity distributions (left) and internal energy distributions (right) of ejected molecules following a 6 km/s impact at $t = 100$ ps. The internal energy distributions were calculated after subtracting streaming velocity and a Gaussian fit was used to estimate the average values.

from the molecular layer–gas interface and the remaining part causes ejection of molecules and/or clusters into the gas phase. Collisions between molecules at neighboring layers lead to the characteristic velocity distribution after ejection. Thus, a few picoseconds following a 6 km/s impact, a broad velocity distribution of ejected molecules is observed, Figure 5 (top left panel). This broad velocity distribution incorporates three peaks at 2, 3 and ~ 5 km/s in the case of TNT; however, the size of the system used in the present simulation does not allow statistically meaningful assignment of such features. The average velocity of molecules that originate from the outermost layers is the highest, reaching the velocity of the impacting piston (6 km/s). The slower molecules observed originate at deeper locations in the adsorbate layer. The same simulation was repeated for a multilayer of benzene molecules with very similar results concerning the ejected molecules velocity distribution; see the bottom left panel in Figure 5. The main goal in performing the simulation with benzene molecules is to examine the influence of the strength of intermolecular binding on the outcome. As can be seen in the two panels in the left column in Figure 5, the velocity distributions are very similar, in both cases they are very broad and in both a resemblance to a three peaks structure can be observed. The main difference is that the lowest velocity peak in the case of TNT occurs at higher velocity (2 km/s) than that for benzene (1 km/s) and that the velocities of fastest benzene molecules are larger (>6 km/s) than the impact velocity. Both phenomena are related to the much stronger intermolecular binding in the TNT multilayer. It is noteworthy to mention that for the lowest impact velocity that lead to intact molecules ejection (3 km/s), the fastest molecules acquire a velocity of ~ 3 km/s, while the majority of the molecules (that originate from deeper layers) are much slower. Thus, the expected velocity distribution for this case approaches the distributions observed in the experiment. The experimental velocity distributions for benzene are also very broad with three peaks at ~ 200 , ~ 500 , and ~ 1000 m/s. The calculated highest velocities in the case of 3 km/s impact on a benzene multilayer are about ~ 1.5 –2 times larger than those observed experimentally. This discrepancy between calculated and measured range of velocity distributions may be attributed to various sources. One possibility is that the limited size and time scales in the simulations underestimate the amount of interparticle (molecules and different size clusters) collisions during the plume expansion and lead to an extended high velocity tail. Another possible explanation is that the experimental set up leads to velocity measurement of

ejected particles from a limited solid angle (with respect to the laser beam and the normal to the substrate, whereas the calculated distribution has contributions of all ejection directions. In any case, there is a good qualitative agreement between the two with only slight quantitative differences.

Subtracting the stream velocity from each ejected molecule, allows to obtain the internal energy distributions of the desorbing molecules, presented in the right column panels of Figure 5. The two internal energy distributions obtained were fitted by Gaussian function to obtain a corresponding effective temperature. These temperatures are a measure of the amount of energy channeled into molecular vibration, bending and rotational degrees of freedom. The panels in the right column of Figure 5 present the internal energy distributions (in K units) of the ejected molecules at the end of the simulation, $t = 100$ ps. It was found that the ejected TNT molecules correspond to a Boltzmann temperature (average internal energy) of 865 K while benzene molecules are much colder, 442 K. As was described above, the absolute majority (93%) of molecules in the 6 km/s impact simulations remain intact and do not decompose. Lower piston impact velocities, 3 km/s, lead to ejection of molecules with internal energy distribution that corresponds to lower Boltzmann temperatures of ~ 450 and 100 K for TNT and benzene, respectively. Following the impact, energy from the shock wave formed can be transferred into internal degrees of freedom. The amount of energy channeled into internal degrees of freedom is expected to depend on the amount of energy transferred during the impact and strength of the interaction among neighboring molecules that is responsible on inter- to intramolecule energy transfer. A direct measure of the strength of interaction among molecules in a solid is the sublimation enthalpy. The calculated sublimation enthalpies of TNT and benzene, 20.2 and 11.1 kcal/mol, respectively, compare well with the corresponding experimental values: 25.1 and 10.7 kcal/mol. These sublimation enthalpies suggest that shock wave energy will be channeled into internal molecular energy more efficiently for TNT as compared to benzene. The reduction of piston velocity from 6 to 3 km/s results in a 4-fold decrease in the transferred energy and, hence, to a reduced Boltzmann temperature of both films.

III. Vibrationally Assisted DIET. Arnolds and co-workers suggested a vibrationally assisted Desorption Induced by Electronic Transitions (DIET) mechanism to explain their experimental observations. They focused in their model on a monolayer of benzene on Pt surface, since no adsorbate coverage dependence was observed in the experiments.⁶ In the proposed model, it is assumed that a photon leads to vibrational excitation of the benzene-Pt system, populating a vibrationally excited state ($v = 4$). This excitation is followed by a second step of electronic transition of the vibrationally excited benzene-Pt bond to the lowest antibonding state. This excited state becomes within reach of the 1.55 eV of photon energy. The transition from the antibonding state back to the ground state involves the ejection of molecules with a translational energy of ~ 0.35 eV (~ 1100 K), matching one of the velocity features (hyperthermal) observed in experiment (for benzene this results in a velocity of 0.94 km/s).

In order to assess the validity of the vibrationally assisted DIET mechanism in the case of TNT, we have conducted simulations where a piston velocity of $v_{\text{imp}} = 1.29$ km/s was used as described below. This corresponds to a kinetic energy of 2 eV, a value higher than the photon energy of 1.55 eV. In the aforementioned mechanism this sets an upper bound for

the piston velocity. Moreover, it was assumed that every molecule in the monolayer has absorbed a photon.

In the initial simulation a multilayer composed of 13 ML of TNT molecules was used as the target sample. The monolayer next to the substrate was assumed to become excited by 2 eV that were added to the translational motion of each molecule in the layer, thus following a DIET like process with 100% yield. This monolayer served as the piston in these type of simulations. The piston impact relaxed rapidly due to fast energy equilibration among all layers in the target. No ejection of isolated molecules or clusters was observed. Next, the target thickness was reduced down to 1 ML to check if molecular ejection occurs for thinner samples. However, even for a single TNT layer, the piston impact was not sufficient to induce any ejection of isolated molecules. The piston energy in the multilayer case resulted in the dissipation of the piston's energy into the TNT film internal degrees of freedom. For the monolayer case, forward motion of the whole layer with some internal heating was observed. The rate of equilibration was found to decrease linearly with the number of TNT layers used (see Figure S2 in the Supporting Information).

Similar calculations were performed for 13 ML of benzene. For velocities of 6 km/s, ejection of single molecules was observed. However, for piston velocity of 0.94 km/s (corresponding to 0.35 eV estimated by the vibrational assisted DIET model) up to 2 km/s, no molecules were ejected.

Evidently, below piston velocities of 3 km/s, the impact energy is insufficient for ejection of intact molecules from the outermost layer. We stress that the calculations reported above correspond to an upper limit of the effectiveness of the DIET process, since the simulation assumed that all impacting molecules were ejected with identical velocity of 1.29 km/s, whereas the probability of the DIET process is prohibitively lower than unity. This is consistent with our earlier result (subsection II) where we have revealed that the minimal piston velocity to cause ejection of intact TNT molecules is 3 km/s.

DISCUSSION AND CONCLUSIONS

According to the proposed model, laser generated plasma plume leads to a mechanical impact on the target thin film forming a shock wave that moves across the film. The current study employed reactive molecular dynamics simulations of a piston impact on thin layers of 2,4,6-trinitrotoluene (TNT) and benzene, used here as model samples. The resultant shock wave propagates at supersonic velocities and leads to ejection of both intact isolated molecules and molecular clusters from the free surface to the vacuum. The process is governed by four consecutive time scales, namely:

(a) Generation of a plasma front at the metal–substrate interface due to the high intensity (10^{13} W cm $^{-2}$), femtosecond nonresonant, laser pulse. The time scale for this process is dictated by the pulse duration (~ 70 fs).

(b) The generation of a shock wave in the film of target material. Shock velocities vary between the minimal velocity to sustain a shock wave ($v_{\text{shock}} >$ longitudinal velocity of sound) and the maximum velocity before significant chemical decomposition of the ejected material occurs. The time scale for the shock propagation duration is roughly 1–2 ps.

(c) Ejection of hot molecular TNT clusters as well as intact molecules from the free surface near the target–vacuum interface.

(d) Disintegration of the clusters by ejection of isolated molecules. This time scale depends on the initial impact velocity and varies between 1 and 2000 ps.

The qualitative features of the proposed mechanism correlate well with available experimental findings, including the generality of intact molecule ejection in a wide range of different substrate materials. Since organic molecules are held together mainly by van der Waals interactions or hydrogen bonding, all types of thin adsorbed layers (crystalline, liquid or polycrystalline) will display the same behavior with minor variations. Another point for which good agreement between the theory and experiment is observed is the velocity distribution of the ejected molecules. In the case of TNT, the ejected molecules velocities are distributed in the range 2–6 km/s for 6 km/s piston impact with a broad velocity distribution that exhibits two velocity features. Benzene, whose cohesive energy is about half of that of TNT, displays three velocity features as is observed in experiments.^{6–8}

Our simulations suggest the existence of an opportunity window of 3–6 km/s of the plasma front velocity in which mainly intact molecules are ejected. Below this range mainly molecular clusters will be generated and at higher impact velocities mainly decomposition products are expected to be observed. This range is characteristic of the lower bound velocity of the plasma plume following ultrashort laser ablation of stainless steel. This mechanism thus allows to relate the impact velocity to the pulse energy and type of substrate material. Thus, allowing the tuning of experimental parameters toward higher yields of intact molecules ejection and easier detection. Indeed, the proposed mechanism should also be valid for other types of substrates provided the laser intensity is sufficient to generate a mild plasma (10^{13} W cm⁻² for most metals and dielectrics). The energy absorbed by the shock wave (E_0) is proportional to the laser fluence, and the upper bound plume velocity scales as $V \propto E_0^{1/2}$; thus, a straightforward method to check the validity of the proposed mechanism would be to compare the upper bound velocities (i.e., velocities obtained following highest impact velocity not leading to chemical decomposition) of the ejected molecules for different substrate materials. From highest to lowest, the ablation thresholds order of stainless steel, silica glass and platinum is silica > SS > Pt. Hence, we predict that the upper bound velocities of the ejected molecules for these substrates to be ordered accordingly, namely: $V_{\max}(\text{silica}) > V_{\max}(\text{SS}) > V_{\max}(\text{Pt})$.

The calculations described invalidate the vibrationally assisted DIET model as the mechanism of leading to molecular ejection. The main reason being that insufficient amount of energy can be deposited at the adsorbate–substrate interface for molecular ejection to occur. This was validated by our simulations of impact on benzene as a target composed of both 1–13 ML and an impact velocity of 0.94 km/s corresponding to kinetic energy of 0.35 eV of ejected molecules. In addition, this mechanism cannot explain the molecular properties such as the generality of the reported experimental results, since DIET is not universal and it is strongly dependent on the position of the excited state. The main difference between our model and that of Arnolds et al. is in the first step (ablation or DIET). We use a quantitative model for both the shock propagation stage and the ejection stage.

■ ASSOCIATED CONTENT

§ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b03711.

Computational details and additional calculations (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank Robert J. Levis for many fruitful discussions. This material is based upon work supported by the U.S. Department of Homeland Security, Science and Technology Directorate, Office of University Programs, under Grant Award 2013-ST-061-ED0001. The views and conclusions contained in this document are those of the authors and should not be interpreted as necessarily representing the official policies, either expressed or implied, of the U.S. Department of Homeland Security.

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