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Photochemical fragmentation processes in laser ablation of organic solids

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Abstract

Studies on ultraviolet (UV) laser ablation of molecular solids have received considerable attention due to its proven and potential applications. Despite its active practical use the mechanisms of laser ablation are still being studied and debated. One crucial mechanistic discussion is on the relative importance of direct photodissociation of chemical bonds versus thermal ejection following rapid conversion of light energy into heat in the ablation processes. It is generally believed that these two processes are coupled in UV ablation resulting in difficulty in analyzing the relative importance of the two mechanisms. In the simulations presented here the breathing sphere model is enhanced allowing the photon absorption event to break a bond in the molecule and then have subsequent abstraction and recombination reactions. The initial system to model is chlorobenzene. Chlorobenzene is chosen because of simplicity of its fragmentation, entailing exclusively scission of the carbon–chlorine bond to yield phenyl and chlorine radicals. The results from the simulations allow us to study the photochemical events and their coupling with the thermal processes. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Ultraviolet (UV) laser ablation of molecular solids has raised considerable interest due to its proven and potential applications in laser surgery and mass spectrometry. The physical processes involved in laser ablation are extremely complex and a detailed understanding of the undergoing processes remains a challenge. It is generally accepted that the absorption of UV photons results in electronic excitation of molecules. The excited molecule can then undergo decomposition, which would be a purely photochemical reaction. Alternatively, the excited molecule can undergo internal conversion to a vibrationally excited ground state and transfer the absorbed energy into thermal energy of the molecular solid.

It is well established that photochemical reactions can play a major role in far-UV ablation of

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polymers and biological tissue [1,2]. The role of the photochemical reactions in the cases when photochemical processes are closely coupled with thermal processes, as for 248 nm irradiation, however, has not been clarified yet. For example, Srinivasan and Ghosh [3] reported the ablation of liquid benzene by a 248-nm pulse, ascribing the phenomenon to photochemical decomposition following two-photon absorption. On the other hand, Buck and Hess [4] pointed out on the importance of thermal processes in their investigating of ablation of benzene film using the same excitation wavelength. Tsuboi et al. [5,6] reported on the 248-nm laser ablation of liquid toluene and benzyl chloride. They concluded that the ablation of toluene is induced by explosive boiling, however, the ablation of benzyl chloride is triggered by the photochemical reaction leading to benzyl radical generation.

In the photochemical processes the photon absorption event break a chemical bond within a molecule forming molecules with smaller number of atoms. The resulting photoproducts occupy a larger volume and create pressure inside the irradiated volume that can then convert to the translational energy of ablation [2]. In previous theoretical efforts to model photofragmentation processes, an increase of the volume occupied by the reaction products has been simulated by the increase of the equilibrium radius of the excited molecules [2,7]. In the model presented here we introduce every reaction product as a spherical particle with its own computational parameters. This approach will allow us to study the dynamics of the photoproducts and to make a direct comparison with experimental observations.

In this paper, we apply this approach to laser ablation of chlorobenzene. Chlorobenzene is chosen because of the simplicity of its photofragmentation, entailing exclusively scission of the C–Cl bond to yield C_6H_5 and Cl radicals, which in solution and static gas cell experiments react with the precursor molecule to form a number of different products [8]. The photochemistry of C_6H_5Cl has been widely investigated in the past several decades [9,10]. It is generally accepted that the compound efficiently undergoes photodissociation reactions by UV light excitation even in the condensed phase as $\mathrm{Ph{-}Cl} \rightarrow \mathrm{Ph}\bullet + \bullet\mathrm{Cl}$ ($\mathrm{Ph} = \text{phenyl}$). By examining a C_6H_5Cl molecular beam [11] it was found that excitation of chlorobenzene by 248-nm laser light takes place through photochemical dissociation and vibrational excitation channels. It was calculated that 36% of the molecules are photofragmented with available energy for photofragments of 19 kcal/mol. In the ablation of neat C_6H_5Cl films [12–14] two fluence ranges were found in which photolysis of chlorobenzene proceeds at very different yields. At low fluences the photolysis yield was found to be an order of magnitude lower than that in the gas phase and desorption of only one new photoproduct, HCl, was observed. Significant fragmentation in the ablation of C_6H_5Cl films was reported only at higher fluences and additional photoproducts, namely Cl, $C_6H_4Cl_2$, $C_{12}H_9Cl$, $C_{12}H_{10}$ and $C_{12}H_8Cl$ were detected.

In the following section a detailed description of the photofragmentation model is presented. The model is then applied for the investigation of photofragmentation processes and their role in laser ablation of chlorobenzene films.

2. Computational model

Our group has developed and applied a molecular dynamics model to study microscopic mechanisms of laser ablation [15–17]. This model is based on the fact that molecules in organic solids have a tightly bound internal structure and form a weakly bound external structure. This feature distinguishes molecular solids from other forms of solid matter and allows one to treat the external and internal molecular motions separately. In the model each molecule can be represented by a single particle that has the true translational degrees of freedom but an approximate internal degree of freedom. The internal breathing mode allows us to control the rate of energy transfer from the exited molecule to the remaining solid. This approximation permits a significant expansion of the time and length scales of the computer simulation yet still allows reproduction of a realistic rate of energy relaxation of excited molecules. The full details of the model are described elsewhere [15].

In the previous simulations by our group [15–18] it was assumed that each excitation event increased the kinetic energy of the breathing mode of the molecule by an amount equal to the photon energy, thus the vibrational excitation of the molecules (i.e., thermal events) in the system has been modeled. Since both photochemical and thermal processes are interrelated to each other and cannot be separated in real systems, it is important to study the photochemical decomposition of excited molecules within the model.

Ablation of chlorobenzene has been chosen to be an initial system for modeling photochemical events. Experimental data from 248-nm laser ablation of chlorobenzene are used as guidelines in choosing the simulations conditions. A set of parameters (molecular mass = 112.56 Dalton, equilibrium radius of the spherical particles representing molecules in the breathing sphere model = 1.59 Å, equilibrium distance between particles = 3.0 Å, density of the molecular solid = 1.064 g/cm^3) are chosen to represent a chlorobenzene solid. The laser irradiation is simulated by excitation of molecules that are randomly chosen according to Beer's law during the time of the laser pulse and for a given fluence. As detected by experiment [12–14] 7% of the excited molecules are photofragmented into two radicals. The choice of radii, positions and intermolecular potentials of Cl and C_6H_5 radicals is based on the value of available energy for photofragments of 19 kcal/mol [11].

On the basis of the solution chemistry of chlorobenzene, the process of dissociation can be followed by the various abstraction and radical–radical recombination reactions. The reactions we have considered in the model are as follows [19]:

$$C_6H_5Cl + \bullet Cl \rightarrow C_6H_4Cl\bullet + HCl + 10.8\ \text{kcal/mol}, \quad (1)$$

$$C_6H_5Cl + C_6H_5\bullet \rightarrow C_6H_4Cl\bullet + C_6H_6 + 11.0\ \text{kcal/mol}, \quad (2)$$

$$C_6H_5Cl + C_6H_4Cl\bullet \rightarrow C_6H_5\bullet + C_6H_4Cl_2 + 12.5\ \text{kcal/mol}, \quad (3)$$

$$Cl\bullet + \bullet Cl \rightarrow Cl_2 + 57.9\ \text{kcal/mol}, \quad (4)$$

$$C_6H_5\bullet + \bullet C_6H_5 \rightarrow C_{12}H_{10} + 138.8\ \text{kcal/mol}, \quad (5)$$

$$C_6H_4Cl\bullet + \bullet C_6H_4Cl \rightarrow C_{12}H_8Cl_2 + 114.4\ \text{kcal/mol}, \quad (6)$$

$$C_6H_4Cl\bullet + \bullet C_6H_5 \rightarrow C_{12}H_9Cl + 114.4\ \text{kcal/mol}, \quad (7)$$

$$C_6H_4Cl\bullet + \bullet Cl \rightarrow C_6H_4Cl_2 + 89.9\ \text{kcal/mol}. \quad (8)$$

Other reactions, responsible for the formation of various photoproducts, are not energetically favorable and are observed neither in the gas-phase nor solution chemistry of the compound.

The probability of the above reactions is set in the following way. When the parent molecule breaks up into chlorine and phenyl radicals, these radicals will try to recombine with another radicals via reactions (4)–(8). If during a certain time, t_1, dissociation products will not meet free radicals to undergo recombination reactions, then they abstract hydrogen atoms from the nearest chlorobenzene molecule. The average lifetime of the radical is about 10^{-12} s [20]. In terms of the reactivity of the hydrogen atom abstraction, the chlorine radical is 2.7 times more reactive than phenyl radical [21]. Therefore we assume than chlorine radical undergoes abstraction reaction (1) after $t_1 = 0.3$ ps. Phenyl radical undergoes abstraction reaction (2) after $t_1 = 0.8$ ps. Based on the exothermicities, we have assumed that the chlorine atom abstraction reaction (3) is more probable than hydrogen abstraction reaction (2). Therefore the product radical $C_6H_4Cl\bullet$, which is less reactive than phenyl radical, will abstract chlorine atom from the parent molecule after $t_1 = 0.7$ ps.

All molecules are represented by spherical particles with its specific mass and interact with each other via the intermolecular pair potential with individually set parameters. Radii and initial positions of various species are chosen to control the available energy of reactions.

3. Results and discussion

To test the model and the reaction probabilities, simulations for a 3D solid chlorobenzene sample, consisting of 27,600 molecules, are performed. The laser irradiation is simulated by excitation of random molecules during the 15 ps laser pulse at a wavelength of 248 nm. About 7% of the excited molecules are allowed to break into fragments. The laser fluence is kept sufficiently low such that no ablation occurs, only desorption.

The dynamics of the photoproduct formation at low laser fluences is shown in Fig. 1. During the laser pulse the parent molecule breaks up into chlorine and phenyl radicals. The chlorine radical can recombine with other radicals via (4) and (8) or abstract a hydrogen atom from the parent molecule via (1) forming an HCl molecule. At low laser fluences the probability of reactions (4) and (8) is very small, therefore, almost all chlorine radicals undergo reaction (1) which gives the sharp initial rise in the HCl curve. No chlorine radicals can be formed after the laser pulse and, therefore, the concentration of HCl molecules reaches a steady-state value. During the laser pulse the rate of benzene formation is less than HCl, because the reaction (2) is less probable than (1) and phenyl radicals formed by photodissociation participate in the formation of C_6H_6 molecules via (2) and $C_{12}H_9Cl$ molecules via (7). The increase of the $C_6H_4Cl\bullet$ profile during the laser pulse is dictated by reactions (1) and (2). This radical mostly reacts through reaction (6) forming $C_{12}H_8Cl_2$ molecules, but can participate in reactions (3), (7) and (8) as well. Reaction (3) produces more phenyl radicals which lead to the increase of benzene and $C_6H_4Cl_2$ concentrations after the laser pulse. Eventually when all the $C_6H_4Cl\bullet$ radicals react, the concentration profiles for all products will be constant. The concentrations of Cl_2 and $C_{12}H_{10}$ molecules from reactions (4) and (5) are less than 0.05% and are not shown in the figure.

From Fig. 1 one would expect to see similar concentrations of the species in the plume of desorbed molecules, where the leading product should be $C_{12}H_8Cl$ followed by C_6H_6 and HCl. In

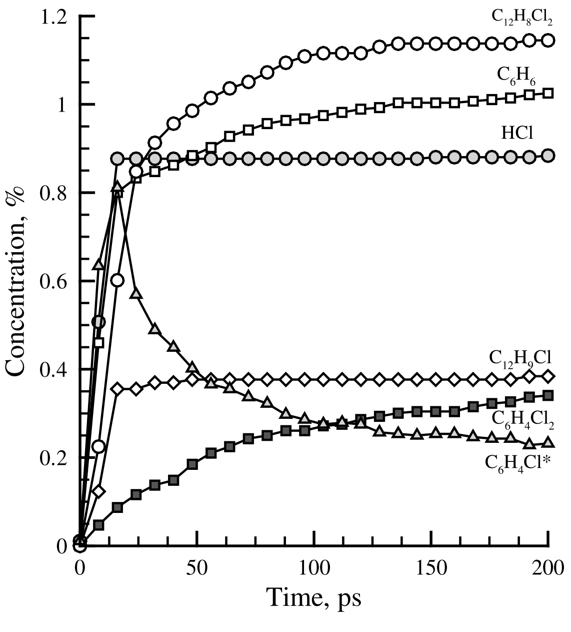

Fig. 1. Concentration of the photoproducts in time at low laser fluence. In addition, the concentration of $C_{12}H_{10}$ and Cl_2 molecules is less than 0.05% and is not shown in the figure.

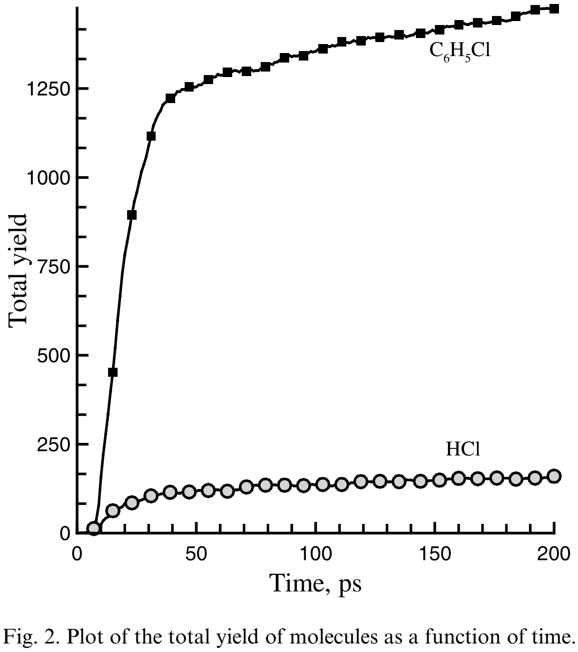

Fig. 2. Plot of the total yield of molecules as a function of time. Other species namely $C_{12}H_8Cl_2$, C_6H_6, $C_6H_4Cl_2$ and Cl are not presented in the plot because of the small concentration (less than 10 molecules).

Fig. 2, however, we can see that mainly chlorobenzene and HCl molecules are ejected, which correlates with the experimental observations. The products such as $C_{12}H_8Cl_2, C_6H_6, C_6H_4Cl_2$ and Cl are not present in the plume in significant amounts. The high ejection efficiency of HCl can be explained by its volatility allowing it to diffuse toward the surface and desorb more easily than other molecules [22]. Other products are bound more tightly to each other and therefore do not eject in any significant numbers.

4. Conclusions

The model shows the potential for the detailed analysis of the photochemical aspects of the laser ablation mechanism. The 3D model incorporates real experimental parameters of the laser ablation process such as pulse width and laser energy, as well as available information on the probabilities and energetics of laser-induced chemical reactions, thus direct quantitative comparisons between computed and experimental results can be made. In future investigations a series of 3D calculations will be performed for a range of laser fluences with an emphasis on making a direct connection with current experimental efforts. The fragmentation yields, ablation threshold, velocity distribution, and the energy content will be compared with the experimental data.

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