Article

The Dependence of CO2 Removal Efficiency on its Injection Speed into Water

Leixi Chen[1], Kimberly Voss[1]
[1] Pittsford Mendon High School, Pittsford, New York

SUMMARY

Scientific research in past decades has come to the consensus that climate change is making drastic alterations to the world we are living in today. Greenhouse gas emission, such as carbon dioxide (CO_2) emission into Earth's atmosphere through burning fossil fuel, is the root cause of this existential threat to humankind. Research and technological innovations are necessary to alleviate the climate crisis. This has prompted us to conduct research to find viable ways of destroying CO_2, such as by breaking the bonds of the CO_2 molecules through high-speed collisions. We hypothesized that injecting CO_2 into liquid water could destroy the molecular bonds. Further, we investigated how fast the injection speed needs to be for effective CO_2 destruction. We used a quantum molecular dynamics (QMD) method to simulate CO_2 collisions with liquid water at a variety of speeds. We collected atomic and molecular positions during and after these collisions through numerical simulations. Analysis of these data suggested that more than 80% of CO_2 can be destroyed if the injection speed is greater than 20 km/s, while lower injection speed is less effective in breaking up CO_2. Our numerical modeling also showed an unexpected result, in that the CO_2 destruction process can also produce hydrogen and CO molecules, which are clean and renewable energy sources. These findings may provide a viable path to mitigate CO_2 emissions into the atmosphere, contributing to solving the urgent climate crisis.

INTRODUCTION

After examining extensive research on climate change, an intergovernmental panel has reported that "it is unequivocal that human influence has warmed the atmosphere, ocean, and land" (1). If governments and societies do not act and encourage technological innovations that help alleviate climate change's impact, the consequences of climate change will only continue to be devasting and will worsen as time goes on (1). One of the most substantial reasons for climate change is the billions of tons of greenhouse gases emitted into the atmosphere every year (1). These emissions of greenhouse gases, such as carbon dioxide (CO_2) and methane (CH_4), mainly come from burning fossil fuels (1). The most common and most damaging greenhouse gas is CO_2, as it is the main contributor to the increasing rate of global warming (1). The powerplant industry in the United States alone emitted around 1.6 billion tons of CO_2 in the year 2021 (2). Globally, there are about 51 billion tons of CO_2 emitted into the earth's atmosphere every year (2). Climate change also produces damage on society, where climate change-induced disasters have led to destruction of infrastructure that will need to be repaired and rebuilt. This societal cost is estimated to be colossal, around $185 per ton of CO_2 (3). These massive amounts of greenhouse gases trap the heat of the sun and continue to warm up the earth at an alarming rate. The most stable CO_2 gases will remain in the atmosphere for many years to come. If this same increasing rate of global warming continues, by the end of the 21st century, it will become hazardous for life on earth.

To eliminate this existential threat to humankind, it is necessary to reduce these emissions (if not to completely stop them) and to remove the existing CO_2 in the atmosphere. Scientific research and technological innovation for CO_2 reduction and storage will be key to avoid disastrous climate repercussions. Over the past two decades there have been many interesting and cutting-edge technologies developed for the capturing of CO_2 to help solve the climate change crisis, such as direct air capture, chemical absorption, and hydrate-based CO_2 capture and storage (4-7). The air capture method, which directly extracts CO_2 from the atmosphere, is in its infancy stage and still has challenges with low efficiency and requirement of storage (4). Chemical absorption uses reactive liquids to absorb CO_2. This method is well studied, however, the additives and chemical agents required for these methods (such as amines) are corrosive in general (5). Thus, we chose not to pursue these two methods. Instead, we started looking into hydrate-based methods, in which water molecules form cages to store CO_2 at high pressure (7.0-20.0 bar) and low temperature (0-4°C) conditions (7). Two key factors for hydrates to be successful are the gas solubility and the contact surface area (7). Our initial simulation of CO_2 and water coexistence indicated that the time it took for the CO2 gas to diffuse into water was too long to be practical. CO_2 prompted us to design and perform numerical experiments on whether injecting CO_2 molecules at certain speed would lead to a quicker way to dissolve and break up CO_2 through collision with water. The main aim of this research was to investigate if CO_2 can be broken-up by a high-speed injection into liquid water and how fast the CO_2 injection speed needed to be in order to efficiently destroy CO_2 after colliding with liquid water.

To the best of our knowledge, this method has not been previously studied. We believe that this simulation scenario could be replicated by experiments in a lab. The mechanism of bond breaking is that due to violent collision, a shocked region is formed in which the electron density is so high that CO_2 bonds are broken due to strong electronic forces. Namely, according to Coulomb's law, the smaller electron-electron distance means a strong repulsive force that breaks

apart the chemical bonds of CO_2. Our numerical experiments for this research used quantum molecular dynamics (QMD) simulations based on density-functional theory (DFT) (8). We used QMD because electrons can only be described by quantum mechanics. The QMD method was invented by Hohenberg, Kohn, and Sham in the 1960s (8,11). Notably, Kohn won the Noble Prize in Chemistry in 1998 for developing the DFT method (8). Such modeling can illustrate the microscopic process of CO_2 injection into water at different speeds. We simulated the chemistry and physics of high-speed CO_2 molecules colliding with liquid water in this project (**Figure 1**). We also tested how collision-induced chemical reactions vary with the given speed of CO_2 molecules. Through these simulations we have concluded that when the speed is larger than 20 km/s more than 50% of CO_2 molecules were broken up.

RESULTS

To learn whether it was possible to break the bonds of CO_2, we used QMD simulations. QMD simulations first take the atomic positions as an input to calculate the electronic density by solving the Kohn-Sham equation (8). The resulting electronic density was used to derive the electronic force on each of the atoms. Together with the ionic force (i.e., the Coulomb force among the ions), the total force is then used to drive atoms to move to their next locations by integrating the Newton's equation in a molecular dynamics step. This QMD procedure can be repeated for thousands of time steps. Time step is defined as a time on the order of femtoseconds, during which the QMD program advances the ion positions. The trajectory of ion movements then provides microscopic pictures of dynamics and chemical reactions occurring in the CO_2-water collisions explored, here (8).

Our numerical experiments were conducted by QMD simulations with water (H_2O) and CO_2 molecules sitting side by side in a box, with periodic boundary conditions applied in all three dimensions (**Figure 1**). The whole system was equilibrated at 300 K with CO_2 molecules given an initial speed varying from 1 km/s to 50 km/s. The QMD simulations typically ran up to 600 fs until the collision process was over. We analyzed the simulation results by identifying the products during and after collisions. The collisions resulted in the dissociation of H_2O and CO_2, leading to the formation of other molecules such as CO, O_2, and H_2. In our numerical experiment, a variety of injection speeds ranging from 1 km/s to 50 km/s were tested. Additionally, we varied the total number of atoms from 222 to 126 in the CO_2 + H_2O system. For different situations of injection speed, we have used different timesteps and simulations times (**Table 1**).

We monitored the number of CO_2 and H2 molecules over time for an injection speed of 20 km/s (**Figures 2a-b**). We found that during the first 100 fs of the collision, the number of CO_2 molecules dropped from an initial value of 30 to roughly 10. Meanwhile, the number of H_2 molecules increased from 0 to around 10. The reactions reached a steady state (oscillating around some average number) after 250 fs. These results showed that high speed CO_2 collisions with liquid water can indeed lead to the destruction of CO_2 and also the production of hydrogen molecules. For a slightly higher injection speed of 25 km/s, the number of CO_2 molecules decreased from 30 to around 5 CO_2 molecules during a period of 600 fs (**Figure 2c-d**). Meanwhile, the number of H_2 molecules produced

reached an average number of 26 molecules. The higher kinetic energy of CO_2 with greater injection speed can break more bonds as the collision is more forceful. A more violent collision will cause a large oscillation in this case (**Figure 2c-d**). At early times when the molecules piled up, the program overcounted the number of transient molecules, because as time went on, we observed the number of molecules dropping; therefore, we disregarded these times that might have faulty data, and only recorded the molecular counting at the later times when there were no more large fluctuations.

Our simulation results at different injection speeds were summarized by a bar graph displaying the percentage of CO_2 left and the percentage of H_2 produced (**Figure 3**). We found that for CO_2 injection speeds larger than 20 km/s, the destruction of CO_2 molecules is incredibly efficient (less than 20 percent remain after the collision). At the same time, H_2 production increased significantly to reach 80% efficiency for an injection speed of 25 km/s. Overall, these QMD simulations indicate high speed (v ≥ 20 km/s) injection of CO_2 into liquid water can be an efficient method for CO_2 destruction, at the same time producing H_2 as a renewable energy carrier. Finally, the number of CO molecules (the byproduct of this reaction) created through these QMD simulations reaches a maximum at the injection speed of 20 km/s while the other byproduct O_2 molecules are increasing with the injection speed (**Figure 4**).

The collision process between CO_2 and water was revealed by snapshots of the QMD simulations for the 10 km/s injection speed case (**Figure 5**). As time proceeded, CO2 molecules started to penetrate into the liquid water (**Figure 5b-c**). In such QMD simulations, the center of mass motion is removed every timestep, so that liquid water molecules and CO_2 are moving towards each other. The removal of center of mass motion is why we saw some empty space in the left portion of the box as time went on (**Figure 5c-5d**). After CO_2 molecules collided with water molecules weak shock was created because the collision speed was larger than the speed of sound in water, which is 1.5 km/s (**Figure 5c**). Then, CO_2 and H_2O molecules started to slowly bounce back from each other (**Figures 5d-5e**). Finally, at t = 501.8 fs, the system had returned to its original configurations (**Figure 5f**). Namely, the CO_2 molecules were moving back to the right portion of the box, while H_2O molecules still filled the left portion of the box, leaving a small H_2O-CO_2 mixing layer at their interface which is slightly different from the beginning. Overall, the simulation results indicated that such a modest collision at this speed (v =10 km/s) breaks only a few CO_2 molecules.

The snapshots from simulations for an increased injection speed of v = 20 km/s indicated that the high-speed CO_2 molecules were being piled up with water molecules at the
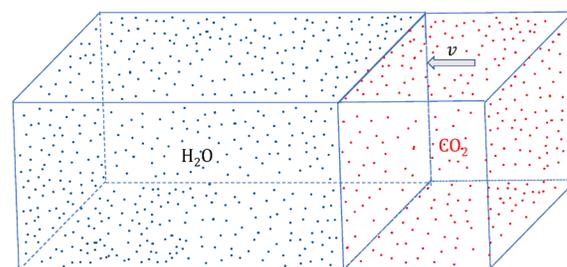

Figure 1: The schematic diagram of a simulation. CO_2 in the right box is injected into liquid water in the left box at different speeds (v).

Velocity (km/s)	Time-step (fs)	Simulation Time (fs)
1	0.5	549.5
10	0.2	501.8
15	0.2	704.4
20	0.1	369.1
25	0.15	587.85
35	0.1	340.4
50	0.04	128.92

Table 1: Simulation time-steps and total simulation times at different injection speeds. The total simulation time was determined by monitoring when the collision had completed. The collision was defined as being completed when the whole system had the molecules randomly distributed within the entire box and the number of molecules produced no longer varied.

interface (**Figure 6**). In fact, such a fast collision induced a strong shock that ends up breaking and destroying CO_2 and H_2O molecules. We found that the shocked region grows as time goes on from t = 53.5 fs to t = 105.4 fs (**Figures 6c-6d**). About 30 fs later, almost all the molecules are shocked (**Figure 6e**). In the shocked region, the electron density is very high, so both CO bonds and HO bonds are broken due to the strong electronic forces. This can be understood from an energy conservation point of view. Namely, when the CO_2 molecules are first injected, they had a large amount of kinetic energy that is turned to a large amount of potential energy after the molecules have collided and been slowed down by H_2O molecules. These potential energies provided an energy source for the breaking of bonds. In the after-

collision situation we saw that the molecules bounced back to fill the whole simulation box (**Figures 6f-6h**). At the end, CO_2 molecules were destroyed (**Figure 6h**); their bonds are broken and different molecules such as CO are created. At the same time, some H_2O molecules dissociated into hydrogen and oxygen atoms, which formed hydrogen and oxygen molecules, as illustrated by the two bonded gray spheres (H_2) and two red spheres (O_2) sticking together.

DISCUSSION

Our work demonstrated that high-speed injection of CO_2 into liquid water has the ability to destroy the molecular bonds of CO_2 and also to generate other products such as H_2 and CO molecules. We employed numerical experiments through QMD simulations to investigate whether high speed injection of CO_2 molecules into liquid water can break up carbon dioxide. By testing different injection speeds, the simulation data suggested that more than 80% of carbon dioxide can be efficiently destroyed for injection speeds larger than 20 km/s. We found that the violent collisions cause the chemical bonds to break not only for CO_2 but also for H_2O, which leads to the creation of hydrogen molecules and other byproducts such as CO and O_2 simultaneously. Both hydrogen and CO molecules may be used as forms of energy carriers (9). In fact, the product, H_2, is a known clean and renewable energy carrier (2). Therefore, we propose that H_2 could provide part of the energy needed to produce such a high CO_2 injection speed. Specifically, hydrogen molecules can deliver or store a tremendous amount of energy and can be used in fuel cells to generate electricity, or power and heat (2). In addition, we also observed other transient molecules, such as CO_3H, OH, C_2, etc. However, our analysis was focused on the long-
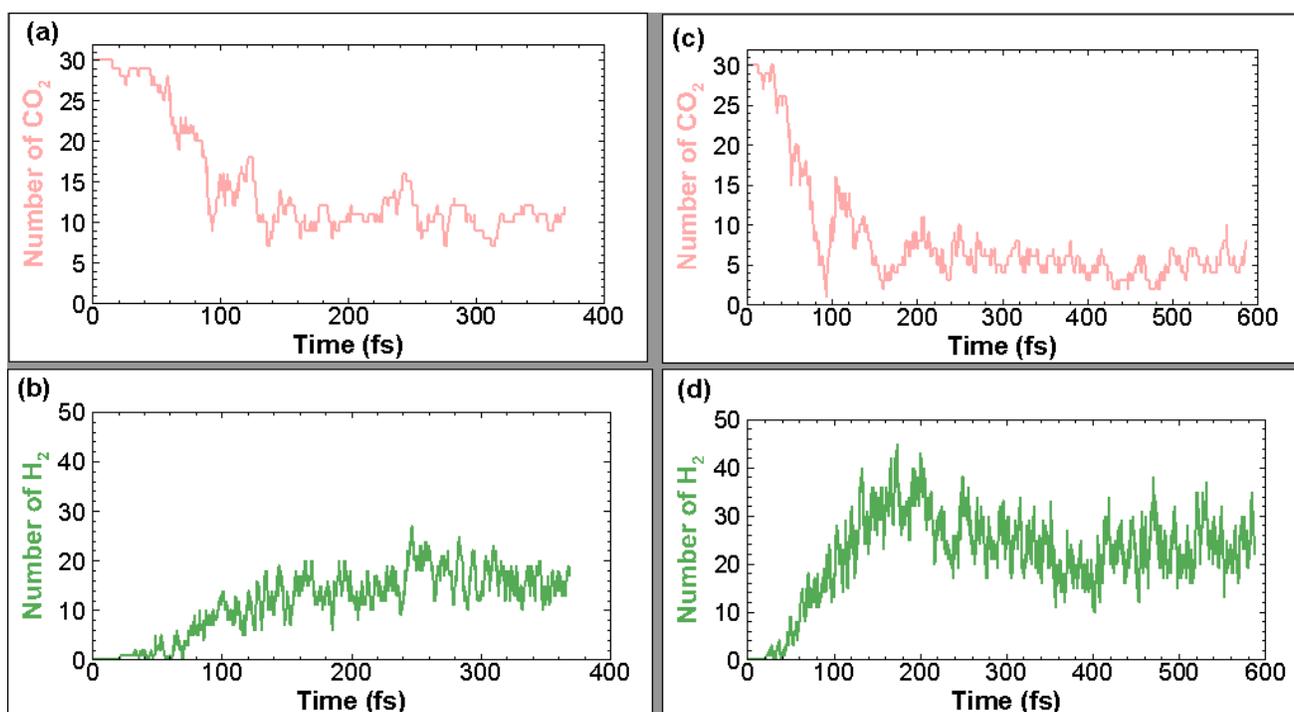

Figure 2: QMD simulation results from a representative run of multiple trials. Number of CO_2 molecules remaining and number of H_2 molecules produced in the simulation box as a function of time, for the case of (a, b) an injection speed of 20 km/s and (c, d) an injection speed of 25 km/s. These results were obtained by molecular counting analysis, which identified the different molecular species at each simulation step.
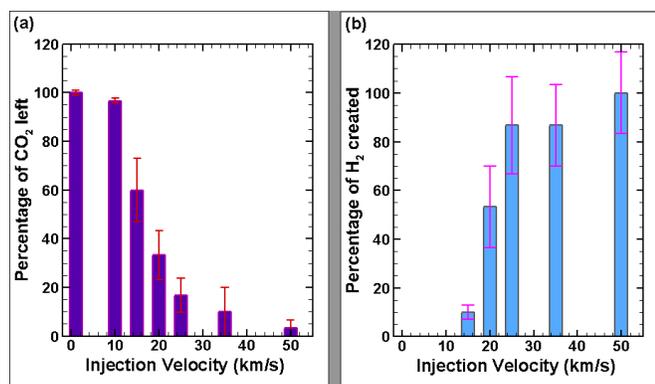
Figure 3: Percentage of byproduct molecules created for different injection speeds. (a) The percentage of (a) CO created and (b) O_2 created after the simulation was run at with injection speeds. The percentage of CO created was defined as the ratio of the number of CO bonds created from the collision, that were recognized by our analysis code, to the original number of CO_2 molecules.

Figure 4: Percentage of byproduct molecules created for different injection speeds. (a) The percentage of (a) CO created and (b) O_2 created after the simulation was run at with injection speeds. The percentage of CO created was defined as the ratio of the number of CO bonds created from the collision, that were recognized by our analysis code, to the original number of CO_2 molecules.

lasting molecules such as CO, CO_2, H_2, and O_2. We define long-lasting molecules as the molecules that were stabilized and stayed together even after the collision was over.

At the lowest speed of 1 km/s, the molecules did not interact/collide at all, leaving all the CO_2 molecules intact (data not shown). When we conducted the collision at 15 km/s, the results we found were somewhat more similar to the case of 20 km/s than to 10 km/s. While the injection speed of 50 km/s was incredibly efficient in destroying CO_2 with 90% removal efficiency, we envision that the energy usage required to power this speed might be too high to be practical in real life situations. We believe that the speed of 25 km/s would be the best to use for destroying CO_2 efficiently because it balances the higher destruction of CO_2 while remaining practical in terms of energy usage.

So far, these simulations were limited to only hundreds of atoms due to computational resources available. Based on the tests we have done with smaller systems, the results indicate that the conclusion from such "numerical experiments" still hold, which suggests our results with hundreds of atoms in our simulation box are convergent. Namely, our findings about high-speed ($\geq$ 20 km/s) injection of CO_2 gas into liquid water should be valid for larger systems.

Our simulations have suggested that the physical mechanism of using high speed injection to destroy CO_2 should work, in principle. However, for practical applications the challenge would be to accelerate CO_2 to such a high speed (>20 km/s). We believe that one solution for high-speed injection of CO_2 may be obtained by pressurizing and quickly releasing carbon dioxide gases. The possible energy consumption for this process could be a limitation for this proposed method. How to solve this secondary challenge associated with energy cost would need to be explored in future studies.

We found that CO and O_2 molecules were produced at injection speeds larger than 15 km/s. We observed that the percentage of CO was highest at around 20 km/s, not at the highest injection speed of 50 km/s. At very high injection speeds, the CO bonds may be broken as well, leading to a
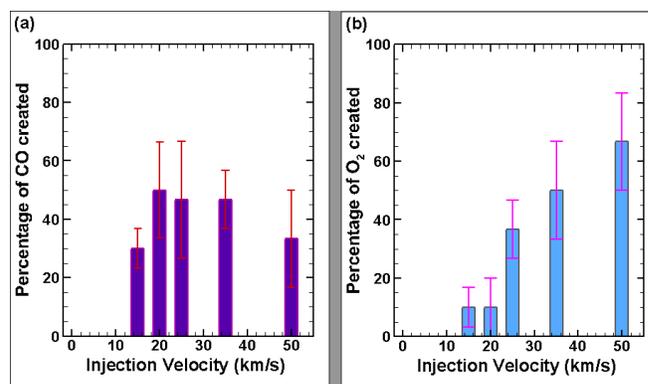
lower number of CO molecules at 50 km/s than at 20 km/s. We also found that O_2 monotonically increased with the injection speed, which we attribute to the greater number of H_2O molecules broken at higher speeds. It is possible that carbon monoxide (CO) could also be used as an energy source as hydrocarbon fuel by combining it with hydrogen or water (9). We envision that it may be possible to use renewable energy to accelerate CO_2 to the high speed that is required in this project. In such a case, this way of accelerating CO_2 will not further produce greenhouse gases. We hope this work will contribute to combating the dire climate crisis.

MATERIALS AND METHODS

Quantum molecular dynamics (QMD) simulations were used to conduct the numerical experiments (10). These simulations were based on density functional theory (DFT) to model quantum many-body electron systems (8,11). For the specific problem, solving the Kohn-Sham equation provided the mean-field method for determining the electron densities of CO_2 and H_2O molecules placed inside the simulation box (8). Once the electron density was determined, the electronic force on each atom of molecules was computed by using the Hellmann-Feynman theorem (10). By adding the electronic force together with the ionic force among ions, the total force to move each atom to its next location was determined by using the total force to solve the classical Newton's equation for a short timestep a new configuration of ions in the box can be obtained. This process was repeated for thousands of timesteps to get the evolution of the system, which was referred to as the molecular dynamics simulation (10). The open source DFT code, Quantum Espresso (12), was used in the QMD modeling of CO_2 injections into liquid water.

Because it was difficult to prepare liquid water in a supercell, the experiment was started by melting the normal ice phase (e.g., the solid phase, *Ih*) with 96 molecules at 600 K. The supercell was composed of 2×2×2-unit cells with 12 H_2O molecules per unit cell in its *Ih*-phase. QMD runs at this high temperature with constant number of particles, constant volume, and constant temperature (NVT) ensemble resulted

in liquid water in a short simulation time. The temperature was then scaled back to 300 K and replicated this supercell one more time to obtain the 192 liquid H_2O molecules for the QMD simulations of CO_2 injection. The 192 H_2O molecules were kept on the left side of a rectangular box, while 30 CO_2 molecules in their gas phase were added in the right portion of the box (**Figure 1**). The rectangular box has a total volume of 42.0 Å x 14.2 Å x 14.2 Å. The system is set up at room temperature of T = 300 K. For a particular simulation all CO_2 molecules were given the same speed pointing towards the box portion filled with liquid water molecules.

In the QMD simulations, periodic boundary conditions were applied. These periodic boundary conditions were applied in all 3 dimensions and allowed molecules to flow in and out of these box boundaries without losing any molecules from the simulation. The PAW (projector augmented wave) potential was used to describe electron-ion interactions. The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional was used for the electron-electron exchange and correlation interactions under the generalized gradient approximation (GGA) (13). The time step for QMD calculations varied from Δt = 0.5 fs to Δt = 0.04 fs, depending on the injection speed of CO2. Smaller time steps were applied for the fast injection speed case, because to follow fast moving atoms a smaller time step was needed. These QMD simulations employed the microcanonical ensemble in which the particle number (N), the system volume (V), and total energy (E) are conserved (*i.e.*, constant) (12). The speed of water molecules had a

Maxwell-Boltzmann distribution with speeds corresponding to the temperature in the box which was set to be 300 K.

For molecular counting, QMD simulated atomic positions were used to calculate the interatomic distances. This was then used to quantify how many CO_2 molecules are destroyed and how many H_2 molecules are formed in these QMD simulations by writing a computer program (Fortran-90). For example, to count how many CO_2 molecules were in a snapshot of a QMD simulation, all carbon atoms were scanned. For each carbon atom, the interatomic distance (RCO) between the selected C atom and every oxygen atom was computed. If RCO was less than the chosen CO bond length of R = 1.6 Å, this was counted as an oxygen atom binding to the selected carbon atom. If the number of oxygen atoms binding to a carbon atom was equal to two, one CO_2 molecule was identified. A bond length of 1.6 Å (about 38% larger than the CO bond length in regular CO_2 molecule) was chosen to account for possible excitations due to the violent collisions. This same method was used to identify other molecules such as hydrogen molecules within a sphere radius of RH-H = 1.1 Å, O_2 molecules within a sphere radius of RO-O = 1.3 Å, and CO molecules within a sphere
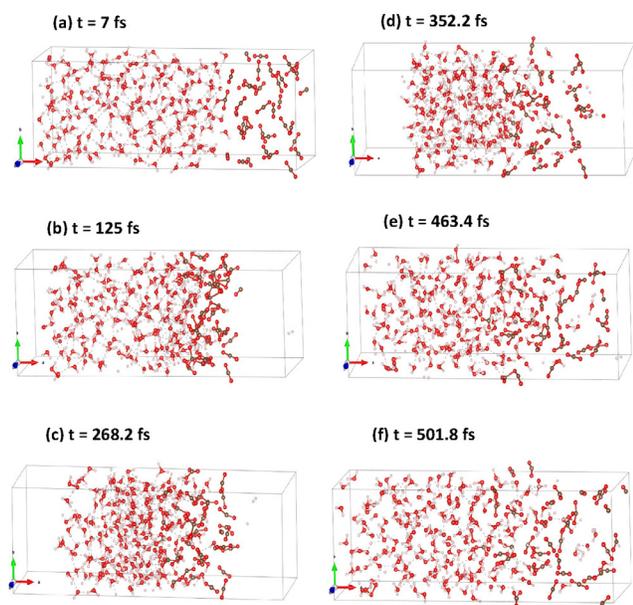

(a) t = 7 fs

(d) t = 352.2 fs

(b) t = 125 fs

(e) t = 463.4 fs

(c) t = 268.2 fs

(f) t = 501.8 fs

(a) t = 0 fs

(e) t = 136.8 fs

(b) t = 23.3 fs

(f) t = 225.1 fs

(c) t = 53.5 fs

(g) t = 274.7 fs

(d) t = 105.4 fs

(h) t = 335.2 fs

Figure 5: Simulation snapshots of CO_2 molecules colliding with liquid water at a speed of 10 km/s. CO_2 molecules were injected into liquid water, which were modeled by density functional theory-based quantum molecular dynamics simulations. Panels show the time progression of the collision. (a) Atom positions are first displayed in the simulation box of the situation at t = 7 fs, even though our simulation starts at t = 0 fs with an MD (molecular dynamic) time step of Δt = 0.2 fs. Hydrogen atoms are represented by light gray spheres, oxygen atoms by red spheres, and carbon atoms by brown spheres. At this early time, the CO_2 molecules were separated from the liquid water molecules, which is how we initially set up the simulation.
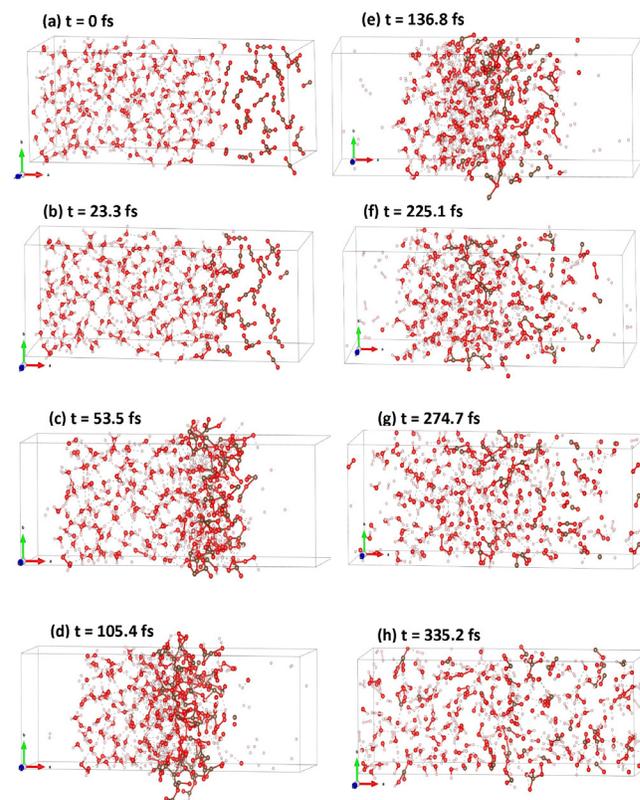
radius of RC-O = 1.155 Å, respectively, as they were possibly formed in the QMD simulation box. The average bond length of C=O is equal to 1.16 Å in CO_2, and the average bond length for H_2 is 0.74 Å at ambient conditions (14). The hydrogen production percentage was defined as the ratio of number of H_2 molecules created at the end of the simulation to the original number of CO_2 molecules to start with. This type of counting was applied to different snapshots to get molecular data (**Figures 3 and 4**). Periodic boundary conditions were taken into account in interatomic distance calculations.

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