Water Splits to Degrade Two-dimensional Group-IV Monochalcogenides in Nanoseconds

Supplementary Information

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Density of water in our simulations

Water has a density of about 1,000 kg/m³ at 373 K and 1 atm pressure.¹ The density of water at the dew (condensation) point at this temperature amounts to 1.5 percent (15000 ppm) volume of air.² At 373 K and 1 atm, the density of air is 1.2 kg/m³ according to both the International Standard Atmosphere and the International Union of Pure and Applied Chemistry, which amounts to 0.02 kg/m³.

A water molecule has a weight of 18 amu or about 3×10⁻²⁶ Kg. In the periodic simulation boxes containing a volume of about 10⁻²⁶ m³, one estimates a density of 3.00 kg/m³, which is three orders of magnitude smaller than liquid water, but two orders of magnitude than the dew point. A volume a hundred times larger, which could be obtained by multiplying the vertical lattice vector by 100 would render a water gas density under standard conditions.
Considering thermal equilibrium, and observing that these molecules traverse periodic images at about every 10 ns, the equipartition theorem implies that a water molecule would reach the simulation subspace in about 1000 ns.

A cursory online search yielded a density of water of less than 1 ppm in a glovebox environment which would translate into presence of a water molecule near the 2D material every 0.01 s (dwell time). Once water is near the group-IV monochalcogenide monolayers, it breaks in less than 20 ns (break time), as demonstrated in the main manuscript.

**Continuity of dynamical variables**

Figure 1 is a zoom-in of all variables listed on Figure 5 of the main text for GeS, showing the behavior at the time resolution of 1 fs near the time of splitting.

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Figure 1: Zoom-in of the time-evolution of energy and structural variables for GeS near the time of splitting.
Process to find the kinetic energy of the oxygen dimer and water, referred to their center of mass

Oxygen dimer

At timestep $i$, the center of mass is given by:

$$r_{cm}(i) = \frac{m_O r_{O1}(i) + m_O r_{O2}(i)}{2m_O},$$

(1)

where $m_O$ is the Oxygen mass, and $r_{O1}(i), r_{O2}(i)$ are the coordinates of the two Oxygen atoms in the dimer at timestep $i$. The relative positions are:

$$r_{rel1}(i) = r_{O1}(i) - r_{cm}(i),$$

(2)

and

$$r_{rel2}(i) = r_{O2}(i) - r_{cm}(i).$$

(3)

The velocity of the atoms in the dimer relative to the center of mass is defined as:

$$\dot{r}_{rel1}(i) \equiv \frac{r_{rel1}(i + 1) - r_{rel1}(i)}{\Delta t},$$

(4)

and

$$\dot{r}_{rel2}(i) \equiv \frac{r_{rel2}(i + 1) - r_{rel2}(i)}{\Delta t},$$

(5)

where $\Delta t$ is the simulation timestep (1 fs).

The instantaneous kinetic energy, relative to the center of mass, reported in Figure 8 and Table 3 of the main text is given by:

$$KE_{O1} = m_O |\dot{r}_{rel1}(i)|^2,$$

(6)
and

$$KE_{O2} = m_O|\dot{r}_{rel2}(i)|^2.$$  \hfill (7)

**Water molecule**

At timestep \(i\), the center of mass is given by:

$$r_{cm}(i) = \frac{m_Or_O(i) + m_Hr_{H1}(i) + m_Hr_{H2}(i)}{m_O + 2m_H},$$ \hfill (8)

where \(m_0\) is the Oxygen mass, \(m_H\) is the mass of Oxygen, and \(r_O(i), r_{H1}(i), \) and \(r_{H2}(i)\) are the atomic coordinates of atoms in the molecule at timestep \(i\). The relative positions are:

$$r_{rel1}(i) = r_O(i) - r_{cm}(i),$$ \hfill (9)

$$r_{rel2}(i) = r_{H1}(i) - r_{cm}(i),$$ \hfill (10)

and

$$r_{rel3}(i) = r_{H2}(i) - r_{cm}(i).$$ \hfill (11)

The velocity of the atoms in the dimer relative to the center of mass is defined as:

$$\dot{r}_{rel1}(i) \equiv \frac{r_{rel1}(i + 1) - r_{rel1}(i)}{\Delta t},$$ \hfill (12)

$$\dot{r}_{rel2}(i) \equiv \frac{r_{rel2}(i + 1) - r_{rel2}(i)}{\Delta t},$$ \hfill (13)

and

$$\dot{r}_{rel3}(i) \equiv \frac{r_{rel3}(i + 1) - r_{rel3}(i)}{\Delta t}.$$ \hfill (14)

The instantaneous kinetic energy, relative to the center of mass, reported in Figure 9 and
Table 3 of the main text is given by:

\[ KE_O = m_O|\vec{r}_{rel,1}(i)|^2, \]  
\[ KE_{H1} = m_H|\vec{r}_{rel,2}(i)|^2, \]  
and

\[ KE_{H2} = m_H|\vec{r}_{rel,3}(i)|^2. \]  

**Details of the creation of movies**

The steps to be followed to create the movie from the ANI file. The ANI format is a concatenation of a sequence of atomistic positions in the \textit{xyz} format, that correspond to atomistic positions throughout the molecular dynamics evolution. The file \texttt{bp.ANI} that contains the trajectory of phosphorene and the oxygen dimer was employed to illustrate the process.

We downloaded the \texttt{md2axsf} utility from:

http://www.home.uni-osnabrueck.de/apostnik/download.html

Then, typed:

```
./md2axsf bp.ANI
```
to create file \texttt{bp.AXSF}.

\texttt{xcrysden} was used to visualize the \texttt{AXSF} file as an animation. We typed:

```
xcrysden --axsf bp.AXSF,
```

The \texttt{xcrysden} GUI window shown as Figure 2 shows the crystal structures of the first frame on the lower left side. A full dial box opens once we click the \texttt{Animated GIF/MPEG/AVI} \texttt{>>} button. Crystal structures will be saved in the working directory, frame by fame, once
the Start Recording Animation button is clicked.

We Click the Start Recording Animation button once again after recording is done. This will bring us to an option where we can save files in AVI format (bp.avi, for example). In order to have compact movie files, we focused the movies on the 2000-frame ranges shown in Table 1. Table 2 shows some parameters employed in xcrysden to create the movies. The avi movies were later converted onto the mpg format.

References

(1) Wagner, W.; Pruss, A. The IAPWS formulation 1995 for the thermodynamic properties of ordinary water substance for general and scientific use. J. Phys. Chem. Ref. Data 2002, 31, 387–535.

(2) Ahrens, C. Meteorology Today, 10th ed.; Brooks/Cole: Belmont, CA, 2012.
Table 1: Movie start and end times for water interaction with phosphorene and group-IV monochalcogenide monolayers.

| Material   | Start time (fs) | End time (fs) |
|------------|----------------|---------------|
| Phosphorene| 10,000         | 12,000        |
| GeS        | 13,546         | 15,546        |
| GeSe       | 10,654         | 12,654        |
| GeTe       | 12,960         | 14,960        |
| SnS        | 2,240          | 4,240         |
| SnSe       | 1,226          | 3,226         |
| SnTe       | 10,000         | 12,000        |
| PbS        | 10,000         | 12,000        |
| PbSe       | 15,423         | 17,423        |
| PbTe       | 10,500         | 12,500        |

Table 2: Various factors to control the ball and bond resolution.

| Element | Chemical connectivity factor | Ball scale factor | Display radius (Å) | Covalent radius (Å) | Ball factor | Ball/stick ratio |
|---------|------------------------------|-------------------|--------------------|----------------------|-------------|------------------|
| H       | 1.30                         | 1.40              | 0.53               | 0.49                 | 0.20        | 0.70             |
| O       | 1.30                         | 1.40              | 1.02               | 0.95                 | 0.20        | 0.70             |
| P       | 1.30                         | 1.40              | 1.40               | 1.35                 | 0.20        | 0.70             |
| S       | 1.30                         | 1.40              | 1.47               | 1.35                 | 0.20        | 0.70             |
| Ge      | 1.30                         | 1.40              | 1.75               | 1.62                 | 0.20        | 0.70             |
| Se      | 1.30                         | 1.40              | 1.61               | 1.49                 | 0.20        | 0.70             |
| Sn      | 1.45                         | 1.40              | 1.80               | 1.80                 | 0.20        | 0.70             |
| Te      | 1.20                         | 1.40              | 1.90               | 1.68                 | 0.20        | 0.70             |
| Pb      | 1.30                         | 1.40              | 1.80               | 1.80                 | 0.20        | 0.70             |
(3) Vigor Tech, Vigor Gloveboxes at a glance. http://www.vigor-glovebox.com/faqs/, 2015 (accessed on July 10, 2018).