Photo-molecular effect (PME) or photon interactions with the air-water interface

1. Basic notions

The photo-molecular effect (PME) name was inspired by the photoelectric effect noted by Heinrich Hertz in 1887 while working with electromagnetic waves in radio domain. The physical explanation of the phenomenon where light can release electrons from a material surface was given by Albert Einstein in 1905. For the first time, Einstein proposed a model where light defined as a corpuscle called photon interacts with matter transferring its energy to an electron bonded into the atomic edifice. If this energy is sufficient, the electron overcomes the attractive forces that hold him into the material and is "emitted" as free particle with a well-defined kinetic energy. These electrons are called photoelectrons.
For this revolutionary ideas, Einstein received the Nobel Prize in 1921 (he had already the general theory of relativity published in 1915!).

Now, the photo-molecular effect means the release of water molecule under the incidence of light. In simpler words, we are looking for an increase in the evaporation rate of water when the air-water interface is illuminated with visible light, especially green light.
When we discuss about water evaporation, the first physical amount which we think at is the specific latent heat needed to change 1 kg of liquid water at atmospheric pressure from liquid to water vapor at 100^0C. And, from the books, this value is 2256 kJ/kg. This is a big amount of energy and immediately we think at thermal evaporation (providing this energy amount via heating process). If we consider the water properties, we will find out that the extraordinary characteristic to take the shape of the vessel it is put in, is due to the hydrogen bonds that connect the water molecules. To get an image a bit more in-depth, we have to start from the structure of water molecule: 2 atoms of hydrogen and 1 atom of oxygen. The molecule of water has a bent structure, which confers to the oxygen atom a partial negative charge and to the two hydrogen atoms a partial positive charge; this charge distribution creates an electrical dipole with a momentum of $\mu = q \cdot l = 6.2 \cdot 10^{-30}$ Cm, where q is the electrical charge and l is the distance between the center of negative charge and the center of the positive charge. The dipole nature within a water molecule creates attractive forces known as hydrogen bonding, allowing them to stick together. Between water molecules, such kind of H-bonds are broken and reformed very rapidly; it was calculated that the H-bonds between water molecules have an average lifetime of 10^{-11} seconds. This explains the property of water to take the shape of the vessel.

Therefore, the water molecules have a tendency to stick together. This is, the so-called cohesive property. And it is the property which allows the water to be pulled through a tube (e.g. capillaries in plants, paper, etc). These forces are when the four H-bonds are possible to be made. But what happens when one H-bond is missing? For example the molecules on the surface of the water do not have other water molecules in all directions - only to the sides and below. The resultant of the three H-bond forces will make stronger the cohesive forces of these molecules on the surface giving the tendency of the fluid surface to shrink into minimum surface area. In other words, at the surface of the liquid, the molecules are "attracted inward" by other molecules located deep in the liquid This is the *surface tension* force. In daily life, this surface tension is very important. The liquid surface will take the shape that corresponds to the smallest local surface area: in this way droplets are formed.

With this knowledge about molecular structures in the water liquid, we realize that a high number of hydrogen bonding in water molecules means it requires a lot of an energy to evaporate one gram of water. The energy is called the latent heat of vaporization. Therefore, a large amount of energy is needed to change water from a liquid state into a gaseous state.

But, studies[1] has shown that the water/air interface is a special place, considering the water structure. It was found that both OH^- and H_3O^+ tend to accumulate in the air−water interface but at a different depth, leading to an ionic double layer distribution at the interface. This tendency arises from the amphipathy of the water self-ions (molecule having both polar (hydrophilic) and non-polar (hydrophobic) domains); the distinct stable solvation structures determine that they preferentially occupy different interfacial depths: hydronium, H_3O^+ , with a strongly hydrophobic oxygen atom is closer to the water surface, hydroxide, OH^- , with a hyper coordination solvation structure prefers to locate at a deeper interfacial depth, and the gap between the two ion layers is only ~4 Å. As compared to H_3O^+, OH^- has a higher interfacial stabilization free energy and consequently a higher concentration in the interface, accordingly to the citated paper. The model developed, is based on local environmental features and does not account for a specific long-range electrostatic interaction term. For further explanation, the reader is invited to investigate the papers citated in this work.

A step further in our understanding the process of evaporation is that the local conditions might produce cleavages between the water bulk and chains of smaller or larger clusters of water molecules interconnected by H-bonds. With an external energy, the smaller number of the H-bonds can be broken and these clusters may leave the water surface, in air (see Figure 1).

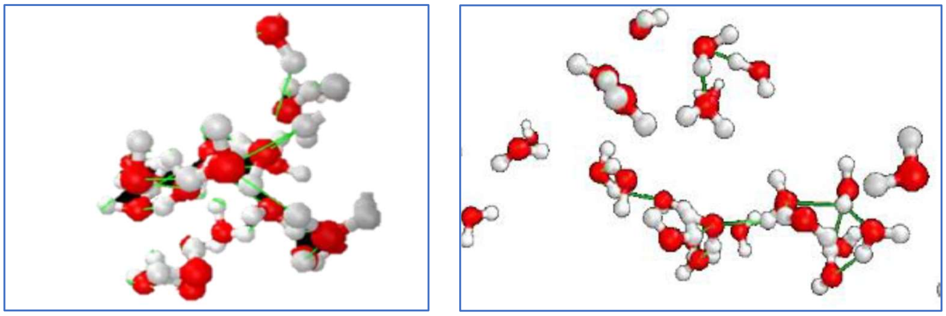

Figure 1. A local cleavage in the huge cluster or water (left) and the broken of the small number of H-bonds that connect a smaller or a larger chain of water molecules to the bulk water (right).

2. PME – the phenomenon physics

When light interacts with air/water interface, the continuity condition for the transversal electrical induction D: $\varepsilon_1 \cdot E_1^{\perp} = \varepsilon_2 \cdot E_2^{\perp}$ (where $\varepsilon_1 = 1$ for air and $\varepsilon_2 = 1.8$ for water in the visible spectrum, and the superscript $\perp$ emphasizes the direction perpendicular to the interface) shows the creation of a huge electrical field gradient. Indeed, at the interface, the electrical field is reduced almost at half in water, and this happens on a few angstroms (~3-7 Å). This electric field will interact with the dipole moments of water molecule, or water cluster molecules. A cluster is formed from water molecules bound between them via H-bonds, while the cluster is connected to the other clusters and/or water surface via van der Waals bonds. The latter is week as ~0.013 eV, while the H-bond in water is 0.21 eV. Measuring the dipole momentum for water molecule ($\mu = l \cdot q$), the charge separation within the dipole can be

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[1] Pengchao Zhang, Muye Feng, Xuefei Xu, *ACS Physical Chemistry Au* 2024 *4* (4), 336-346

calculated[2] as 0.61 Å. These are some speculations to emphases how big the variation in the electrical field might be between the two centers of the charge which form the dipole.
On the other hand, from energy point of view, the photons at 500 nm have an energy of 2.48 eV. Considering the van der Waals bond, one photon can cleave off a water cluster breaking 2.48/0.013=~190 bonds; or 2.48/0.21=~11 H-bonds. The way how this cleavage may happen is a question to be answered.

3. PME - experimental evidences

The experimental setup consists of a green laser (λ=532nm, 50 mW), and an analytical scale, Mettler Toledo, connected on-line with a computer to measure the weight of water droplet at a programable time-interval in this case, at each second). The photo-molecular effect happens when a TM-polarized laser shines on the air–water interface at an angle such that an electrical field component perpendicular to the surface.
We found that there is an optimum incident angle under which the evaporation is maximum;

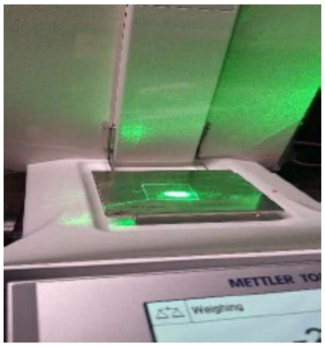

Figure 2. A snapshot during the measurements under the laser beam

In Figure 2 is shown a snap-shot photo during the experiment. I mention that the laser beam has 3-4 mm in diameter. It has to be TM-polarized and must reach the air–water interface at an angle such that the electrical field component is perpendicular to the surface and, it changes rapidly across the interface, leading to a net force acting on polar water molecular clusters (see the explanation from paragraph 2). When the photon energy matches the energy necessary to realize a cleavage off the cluster from its surrounding, the cluster will be driven out of the air–water interface.

4. Measured data and their analysis

Using the analytical scale, the weight of the glass substrate and, at the moment t=0 sec, the weight of water droplet + glass have been measured. Therefore, the mass of the water at the beginning of the experiment is well known. Two types of measurements have been made:

4.1 The laser is OFF at the beginning of the experiment and after a while is turned ON

The mass of the glass substrate was 0.203g, and glass+ water droplet was 0.2446g; this means that we started the evaporation experiment with a mass of water of 0.0416g. For the first 3495 sec the analytical scale monitored the evaporation without the laser beam. The total time of the experiment was 7148 sec. The experimental data are shown in Figure 3.

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[2] *https://water.lsbu.ac.uk/water/water_molecule.html#:~:text=In%20liquid%20water%2C%20this%20gives,molecules%20causes%20its%20polar%20nature.*

We see a clear change in the evaporation rate from $8.6 \cdot 10^{-6}$g/sec without laser beam to $9.2 \cdot 10^{-6}$ g/sec with the laser ON. We mention the fact that these values are calculated for the situations when the evaporation rate is constant. In the last part of the experiment, the evaporation rate decreases to zero. This is due to diminishing the surface of the evaporation.

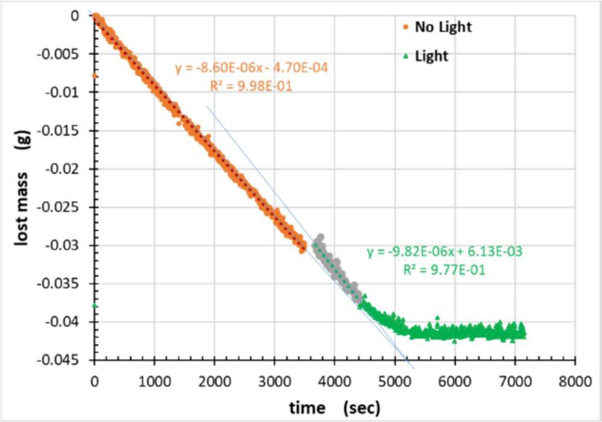

Figure 3. The experiment of water evaporation under the sequences: laser beam off at the beginning, laser beam on at the middle of the experiment time.

4.2 The laser is ON at the beginning of the experiment and after a while is turn OFF

Mass of the glass substrate = 0.2018g, mass water-droplet + glass= 0.2378g, which means the mass of the water droplet at t=0 sec was 0.036g.
The evolution of water mass in time, due to evaporation is shown in Figure 4. The total time of the experiment was 5629 sec and the action of turning OFF the laser beam happed at t=2466 sec.

The evaporation rate under the green light was $9.1 \cdot 10^{-6}$g/sec and respectively $6.97 \cdot 10^{-6}$ g/sec when the laser was turn off. Here the difference in the evaporation rate is notable: under the green laser light the evaporation rate increases with 30%.
A similar behavior, as in the previous experiment, was observed regarding the mass lost in evaporation versus time at the end of the experiment.

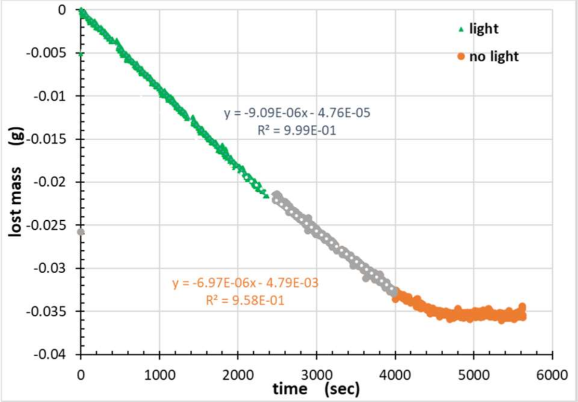

Figure 4. The experiment of water evaporation under the sequences: laser beam on at the beginning, laser beam off at the middle of the experiment time.

5. An unfinished ending

The conclusion of this research is simple: the photo-molecular effect under the **green laser beam** is proved and **has as effect an tremendous increasing in water evaporation with more than 25%,** when comparing with the evaporation rate under the same conditions (temperature, relative humidity) without the laser beam.

If the results of future investigations will be positive, then the reader is facing a revolutionary mode to industrial drying of water-based liquids onto/into solid materials. An example can be the printing industry where water-based ink is jetted on thin porous paper. Matrixes of laser diodes, where each pixel - laser can be individually addressed, with the digital image of the ink droplets onto the paper, can be the future drying mechanism locally, pixel by pixel .