

# Light alkanes physisorption and chemisorption on SnO<sub>2</sub> pyramid clusters surface as a function of temperature: A DFT study

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## ABSTRACT

The results obtained from calculated Gibbs free energy are used to estimate the reaction rate of the physisorption and chemisorption of light alkanes on SnO<sub>2</sub> pyramid surface clusters as a function of temperature. The present investigation includes the interaction of alkanes including methane, ethane, propane, and butane with SnO<sub>2</sub> pyramid surface clusters. The results showed that the reaction rates of physisorbed light alkanes by van der Waals force increase with temperature. However, the physisorption phenomena do not appreciably alter the energy gap that hinders the electrical sensitivity of SnO<sub>2</sub> clusters to light alkanes. On the other hand, chemisorption reactions significantly reduce the energy gap through hydrogen attachment or the replacement of oxygen with hydrogen atoms of alkanes, so that the sensitivity of SnO<sub>2</sub> clusters to Alkan gases is possible. A good agreement was found between the trends of calculated reaction rates and the experimental findings using the Arduino microcontroller.

**Keywords:** SnO<sub>2</sub>, gas sensor, methane.

## Introduction

Tin dioxide (SnO<sub>2</sub>) is one of the most used materials in gas sensing. This material can be used to detect hydrocarbons [1, 2], carbon dioxide [3], hydrogen [4], nitric oxide [5], etc. The present work includes the theoretical calculations of the sensitivity of SnO<sub>2</sub> nanoclusters to light alkanes. All the first four alkanes, i.e. methane, ethane, propane, and butane are in the gas phase at standard conditions [6]. Heavier alkanes are liquid at standard conditions, so they are less important in gas detection. Methane is an ingredient of environmental gases. Methane and other alkanes are mainly used for heating and as a fuel, which can be ignited by the presence of oxygen. They can be distributed as liquids or pressurized gases. As a consequence of their

applications, sensing the existence of these gases in the air is an important operation for safe use and transportation.

SnO<sub>2</sub> nanoparticles are anticipated to be superior in their sensitivity to gases than bulk material because of larger surface area. SnO<sub>2</sub> pyramids are experimentally found on SnO<sub>2</sub> surfaces as a result of surface reconstruction [7, 8]. These pyramids are found stable and able to explain the experimental findings of Indium doped SnO<sub>2</sub> nanoclusters [8]. Moreover, the SnO<sub>2</sub> pyramids show the exact experimental oxygen deficient stoichiometry of SnO<sub>1.8</sub> as in the present investigated cluster (Sn<sub>10</sub>O<sub>18</sub>) [8].

Density functional theory (DFT) application is limited to calculate the interaction of alkanes with SnO<sub>2</sub> structures. The interaction of methane with Sn<sub>1-x</sub>Ge<sub>x</sub>O<sub>2</sub> has been described by Tabata et. al. [9] and the interaction of ethane with SnO<sub>2</sub> (110) surface has been described by Viitala. Theoretical propane and butane interactions with SnO<sub>2</sub> nanoclusters are rarely encountered in literature.

In the present work, the physisorption and chemisorption of light alkanes on SnO<sub>2</sub> pyramid surface clusters as a function of temperature was theoretically investigated using Gibbs free energy of interaction to obtain the reaction rates. The reactions include van der Waals interaction and several H attachments

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and O replacement reactions by alkanes' H atoms. The results were compared with the trends of experimental findings.

## Theory

B3LYP functional is frequently described as one of the successful methods within the framework of density functional theory (DFT) which was used in the present work in combination with the appropriate basis [10]. The best available basis set for the heavy metal Sn is 3-21g. Other atoms are treated with 6-311G\*\* basis set including O, H, and C atoms. molecular vibrational modes and their convergence were also calculated using the Gaussian 09 program to test the stability of the investigated molecules [11]. To calculate reaction rates, Gibbs free energy of various reactions as a function of temperature was calculated. Gibbs free energy takes into account thermal corrections of electronic, translational, vibrational, and rotational molecular degrees of freedom.

All the molecules, encountered in the present work such as tin dioxide cluster (Sn<sub>10</sub>O<sub>18</sub> and butane as in Fig (1)), methane, ethane, propane, and butane were first treated separately including structure optimization, stability, and calculating Gibbs free energy. This procedure was also repeated for the reaction products such as Sn<sub>10</sub>O<sub>17</sub>H, H<sub>2</sub>O, ketones, H<sub>2</sub>, O<sub>2</sub>, etc. Gibbs free energy of the reactions was then calculated as a function of temperature. The reaction rates could then be calculated using Gibbs free energy difference between the products and reactants.

## Results and Discussion

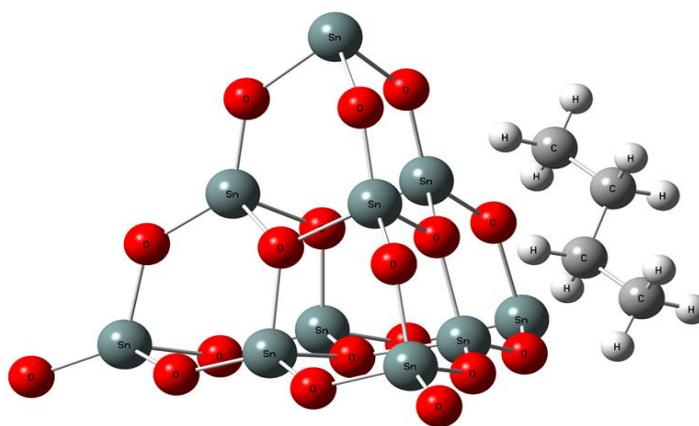
The following reaction probabilities were investigated in the present work:

1. van der Waals interaction of Sn<sub>10</sub>O<sub>18</sub> cluster with alkanes (Fig (1)).
2. The attachment of one hydrogen atom to one oxygen atom at the Sn<sub>10</sub>O<sub>18</sub> cluster surface (Fig (2)).

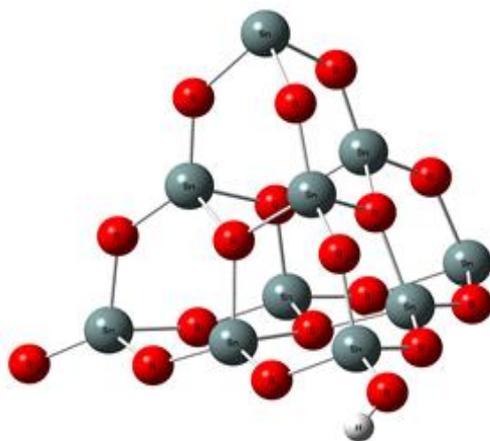
3. The attachment of one hydrogen atom to one tin atom at the Sn<sub>10</sub>O<sub>18</sub> cluster surface (Fig (3)).
4. The replacement of one oxygen atom at the Sn<sub>10</sub>O<sub>18</sub> cluster surface by one hydrogen atoms from the alkane (Fig (4)).
5. The replacement of one oxygen atom at the Sn<sub>10</sub>O<sub>18</sub> cluster surface by two hydrogen atoms from the alkane.
6. The replacement of two oxygen atoms at the Sn<sub>10</sub>O<sub>18</sub> cluster surface by two hydrogen atoms from the alkane.
7. The attachment of two hydrogen atoms from the alkane to two oxygen atoms at the Sn<sub>10</sub>O<sub>18</sub> cluster surface.
8. The attachment of two hydrogen atoms to one oxygen and one tin atom at the Sn<sub>10</sub>O<sub>18</sub> cluster surface.
9. The attachment of two hydrogen atoms to two tin atoms at the Sn<sub>10</sub>O<sub>18</sub> cluster surface.

Except for the first four probabilities, all other reactions were either unstable or less probable or important than the first four reactions. As an example, in reaction number (5) the final molecule, Sn<sub>10</sub>O<sub>18</sub>H<sub>2</sub>, did not geometrically converge using optimization routines in Gaussian 09 program, utilized in the present work. The multiple attachments or replacement reactions as in the case of reactions (5-9) were less probable. The discussion is limited to the first four reactions as in Figs (1-4).

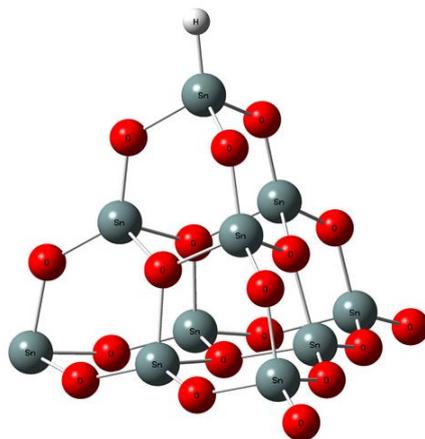
As seen in Table (1) and Fig (5), the formed molecular clusters as a result of alkane reaction with Sn<sub>10</sub>O<sub>18</sub> cluster had different energy gaps than the original cluster. The physisorption of alkanes did not appreciably change the energy gap of the Sn<sub>10</sub>O<sub>18</sub> cluster (Fig (1) and the second row of Table (1)). As a result, the change of the electrical resistivity cannot be used to distinguish the existence of alkanes physisorbed on Sn<sub>10</sub>O<sub>18</sub> cluster surface. On the other hand, chemisorption of the H attachment on the surface Sn atom (Sn<sub>10</sub>O<sub>18</sub> cluster surface) had the largest change in energy gap followed by O replacement by a single H atom. H attachment on the surface O atom (Sn<sub>10</sub>O<sub>18</sub> cluster surface) was also a reaction path that reduced the value of the energy gap even though it reduced the gap less effective than the two chemisorption paths mentioned above.



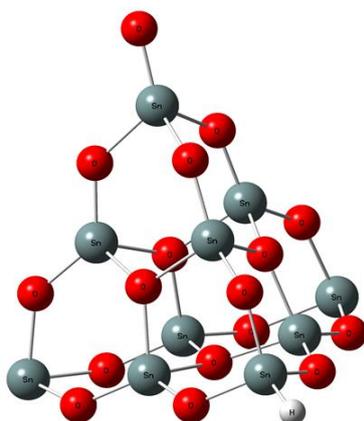
**Figure 1:** van der Waals attraction of butane to the Sn<sub>10</sub>O<sub>18</sub> cluster.



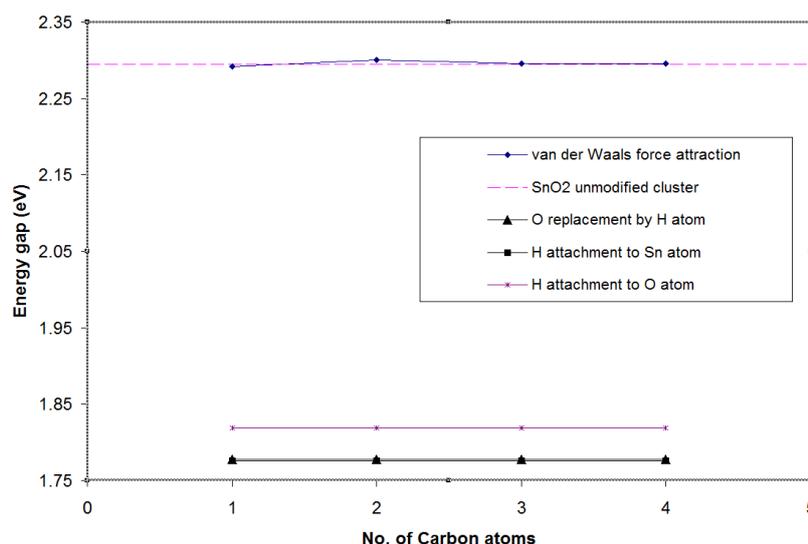
**Figure 2:** Attachment of a single H atom to oxygen atom at the Sn<sub>10</sub>O<sub>18</sub> cluster surface (Sn<sub>10</sub>O<sub>18</sub>H).



**Figure 3:** Attachment of a single H atom to a tin atom at the Sn<sub>10</sub>O<sub>18</sub> cluster surface (Sn<sub>10</sub>O<sub>18</sub>H).



**Figure 4:** Oxygen replacement by alkanes hydrogen atoms (Sn<sub>10</sub>O<sub>17</sub>H).



**Figure 5:** Energy gap of the formed clusters due to different reaction channels of the gas reactions of alkanes with the original Sn<sub>10</sub>O<sub>18</sub> cluster. The dashed line represents the original gap value of Sn<sub>10</sub>O<sub>18</sub> cluster. O replacement reaction overlaps with H attachment to Sn atom reaction in their energy gap values (Table(1)).

**Table 1: Energy gap of Sn10O18 cluster compared with different adsorption cases.**

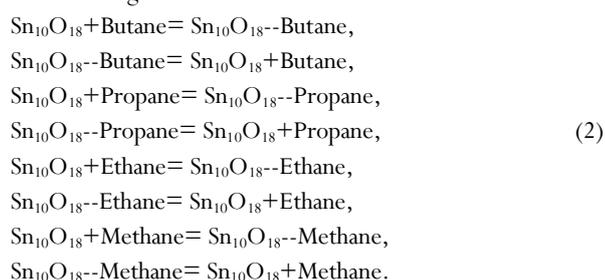
	Molecule	Energy gap (eV)
1	Sn <sub>10</sub> O <sub>18</sub>	2.294
2	Sn <sub>10</sub> O <sub>18</sub> --C <sub>4</sub> H <sub>10</sub> (Fig (1) (van der Waals force)	2.296
3	Sn <sub>10</sub> O <sub>18</sub> H (Fig (2)) (H attachment on the surface O atom)	1.819
4	Sn <sub>10</sub> O <sub>18</sub> H (Fig (3)) (H attachment on the surface Sn atom)	1.776
5	Sn <sub>10</sub> O <sub>17</sub> H (Fig (4)) (O replacement by single H atom)	1.778

Reaction rates can be estimated using calculated Gibbs free energy. The reaction rate ( $k$ ) as a function of temperature ( $T$ ) is given by equation <sup>[11]</sup>:

$$k(T) = \frac{k_B T}{hc} e^{-\Delta G / RT} \quad (1)$$

where  $k_B$  is Boltzmann constant,  $h$  is Planck's constant,  $c$  is the concentration,  $\Delta G$  is Gibbs free energy difference (between products and reactants), and  $R$  is the gas constant.

Fig (6) shows Gibbs free energy of the physisorption reaction via van der Waals reaction of alkanes with the Sn<sub>10</sub>O<sub>18</sub> cluster. The lines in the upper half of Fig (6) represents the attachment reaction of alkanes to the Sn<sub>10</sub>O<sub>18</sub> cluster while the lower half represents the alkanes' removal reaction. The figure represents the following reactions:



The two dashes (--) represent a van der Waals bond. Fig (6) shows that all alkanes have nearly the same value of Gibbs free energy for either attachment or removal reactions. According to Eq (1), the negative values of Gibbs free energy ( $\Delta G$ ) have high values of reaction rates while the positive values of Gibbs free energy have low values of reaction rates. As a result, alkanes' removal is quite faster than attachment to the Sn<sub>10</sub>O<sub>18</sub> cluster. In all the cases, the electrical sensitivity of Sn<sub>10</sub>O<sub>18</sub> cluster to alkanes through van der Waals reaction is quite low compared to other reaction channels as can be demonstrated from the energy gaps of Fig (5) and Table (1).

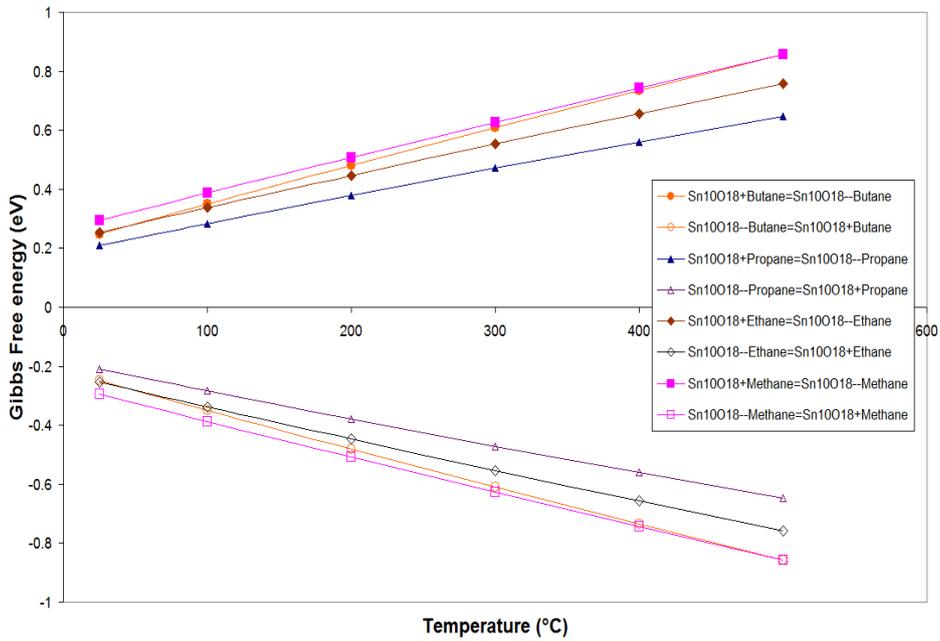
Fig (7) shows Gibbs free energy of chemisorption reactions of the Sn<sub>10</sub>O<sub>18</sub> cluster with butane. The hydrogen attachment reactions appeared now with a negative sign indicating a high reaction rate. The hydrogen removal reactions appeared with a positive sign indicating a low reaction rate. Most of these reaction rates were stronger than physisorption reactions via van der Waals reaction (absolute value of van der Waals reactions are less than 1 eV). The highest reaction rate was for the H attachment on O surface sites. The Gibbs free energy of this reaction was near -3 eV. The other two chemisorption reactions had values between 0.0 and -1.0 eV depending on temperature. These results showed that H attachment on O surface sites is the dominant reaction channel.

Fig (8) shows the reaction rates of the investigated reactions in Fig (7). Because of the negative sign in Eq (1), the H attachment and O replacement reactions were in the upper half while the H removal reactions were in the lower half of the figure.

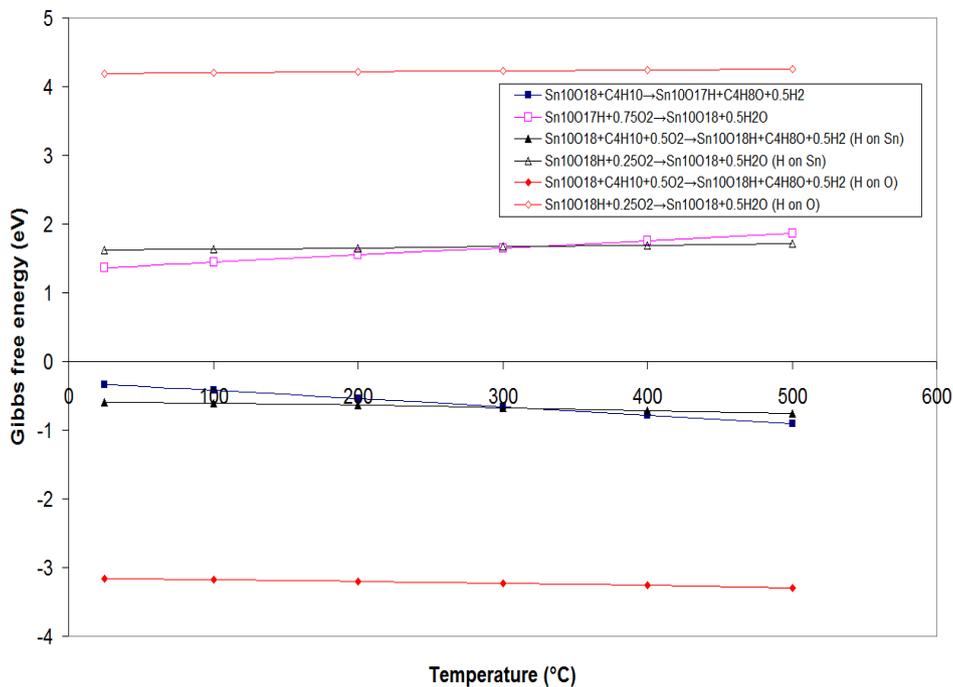
Fig (9) shows the experimental detection of butane using an Arduino microcontroller and MQ-2 gas sensor <sup>[12-14]</sup>. The active material of the MQ-2 gas sensor is a thin layer of SnO<sub>2</sub> <sup>[15]</sup>. We recall from the introduction that SnO<sub>2</sub> pyramids are experimentally found on SnO<sub>2</sub> surfaces as a result of surface reconstruction <sup>[7, 8]</sup>. As the gas sensor is exposed to butane, a sharp increase in the detection of butane appears in a few seconds. As we cut-off butane gas, the concentration of the gas

decreases relatively slowly taking more than 300 seconds to reach undetectable gas concentration. This behavior is consistent with the results of Fig (7) and Fig (8) in which Gibbs

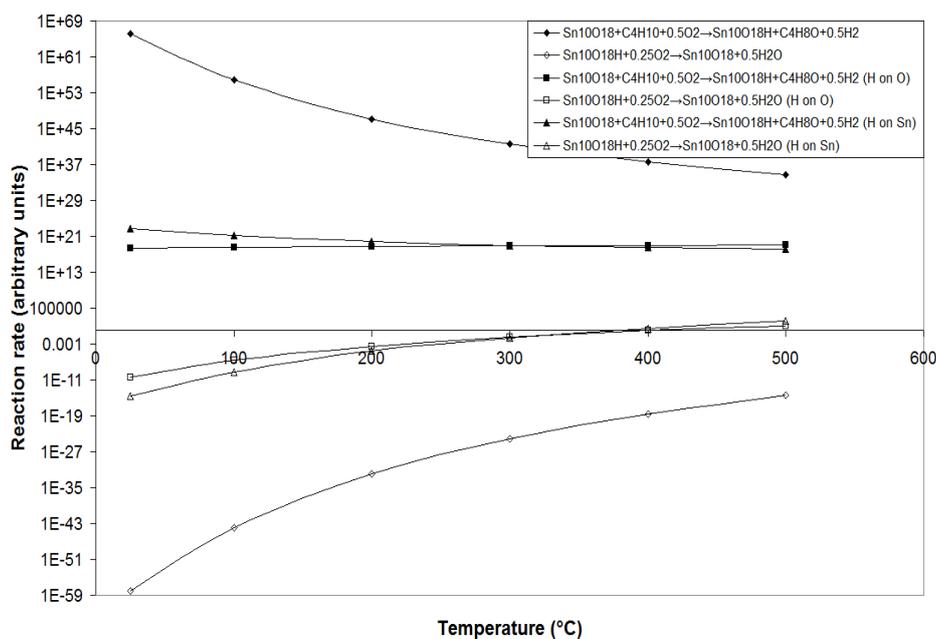
free energy of H attachment is negative indicating high reaction rate with respect to the positive Gibbs free energy of H removal that has slow reaction rate.



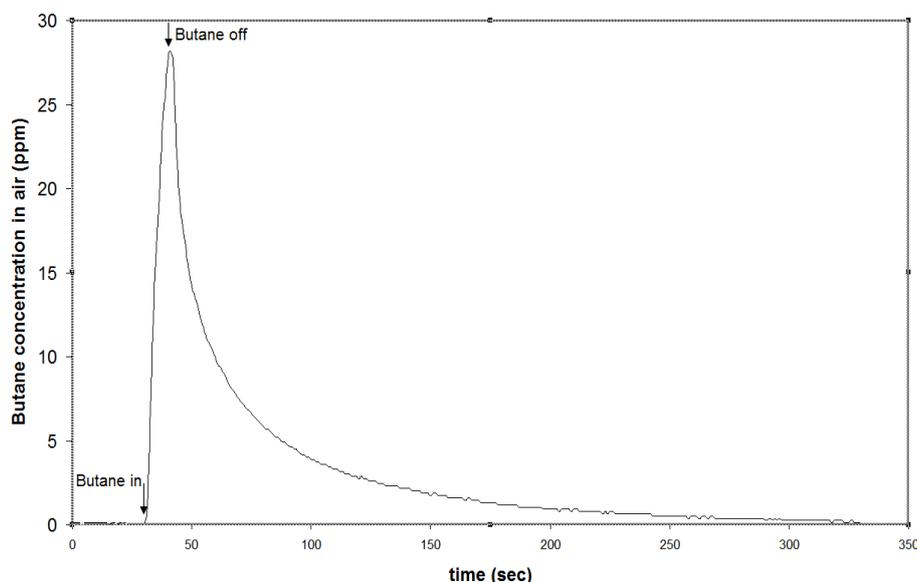
**Figure 6:** Gibbs free energy of van der Waals force bonding with light alkanes. The term Sn<sub>10</sub>O<sub>18</sub>--Butane means that Sn<sub>10</sub>O<sub>18</sub> cluster is bonded with butane molecule via van der Waals force.



**Figure 7:** Gibbs free energy of chemisorption reactions of the Sn<sub>10</sub>O<sub>18</sub> cluster with butane.



**Figure 8:** Chemisorption reaction rates of the Sn<sub>10</sub>O<sub>18</sub> cluster with butane.



**Figure 9:** Experimental detection of butane using an Arduino microcontroller and MQ-2 gas sensor in an open space. SnO<sub>2</sub> surface is the active material in the sensor.

## Conclusions

The results of reaction rates of the physisorption and chemisorption of light alkanes on SnO<sub>2</sub> pyramid surface clusters as a function of temperature showed that the physisorption phenomena have small reaction rates and do not appreciably alter the energy gap that hinders the electrical sensitivity of SnO<sub>2</sub> clusters to light alkanes through physisorption. On the other hand, chemisorption reactions via hydrogen attachment or oxygen replacement by alkanes hydrogen atoms significantly reduce the energy gap with higher reaction rates for the forward reaction and slow reaction rate for the reverse reaction, so that the sensitivity of SnO<sub>2</sub> clusters to alkanes is possible via chemisorption only. The experimental trends using

Arduino microcontroller and MQ-2 gas sensor agrees well with the present reaction rates.

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