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COMMENT

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Reply to the 'Comment on "Quantum interference effects in biphenyl dithiol for gas detection"' by A. Grigoriev, H. Jafri and K. Leifer, *RSC Adv.*, 2020, 10, DOI: 10.1039/C9RA00451C

Jariyanee Prasongkit*

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The Comment on our publication [Prasongkit *et al.*, *RSC Adv.*, 2016, **64**, 59299] is puzzling since it is well known that biphenyl is fairly non-reactive. Hence, it's not surprising we have low binding energies when the gas molecules were adsorbed on biphenyl dithiol (BPDT). The large binding energy of NO_2 chemisorbed onto BPDT (~2.04 eV) in the Comment conflicts with existing theoretical and experimental evidence. Grigoriev *et al.* have attempted to compare their results to our findings, employing different approximation schemes under the density functional theory (DFT) framework. Here, the effect of taking into account van der Waals (vdW) interactions upon the adsorption mechanism of small aromatic molecules has been discussed.

The following points have been made in response to what Grigoriev *et al.* have stated in the Comment (in italic font) and misleading specific claims made in the Comment need to be refuted.

Grigoriev *et al.* claim that: "*We find from our calculations, that the binding energies calculated for the NO_2 molecules are too low, most likely due to the lacking optimization of the site at which the gas molecule binds to the BPDT.*" and "*In fact, our calculations could show that the variation and energy optimization of the binding site of the gas molecule, NO_2 in this case to the BPDT is between 1.04 eV and 2.04 eV large.*".

Most importantly, Grigoriev *et al.* have used a standard generalized gradient approximation of Perdew, Burke, and Ernzerhof (GGA-PBE)[1] functional which has not included van der Waals dispersion correction. The biphenyl is an aromatic hydrocarbon which is rather non-reactive.[2] Thus, a gas molecule interacting with the biphenyl would be complicated due to their weak intermolecular forces including the van der Waals interactions. Several studies[3–5] on the adsorption of small aromatic molecules have been performed including employed the van der Waals correction[6–8] taking into account the weak dispersive interactions to the GGA functional. The non-local van der Waals density functional shows a significant change in the adsorption heights, energies and charge transfer, compared with those obtained from the standard GGA,[9,10] and showed very good agreement with the experimental data.[11]

In our paper, a description of van der Waals (vdW) interactions was included in our calculations using the non-local van der Waals density functional (vdW-DF) of Dion *et al.*[7] The binding energy of NO_2 adsorbed on the BPDT is 0.17 eV, which are in line with the previous studies[12,13] of small molecules adsorbed on aromatic hydrocarbon.

Based on chemical properties of biphenyl, it would be impossible that NO_2 can be chemisorbed onto the BPDT. The large binding energy of NO_2 (~2.04 eV) reported in the Comment probably arises from improper exchange–correlation approximation using the PBE[1] alone. On the use of the GGA functionals, which neglect the van der Waals interactions, can lead to an incorrect description for weak adsorption cases. However, it is surprising that the binding energies, using the standard GGA-PBE for NO_2 chemisorbed on B-doped and N-doped graphene,[14] are only 0.325 eV and 0.260 eV, respectively. Hence, the calculation performed by Grigoriev *et al.* tends to have some methodological problems, producing inaccurate results. Consequently, it is not true when the Comment wrote "*As a consequence, other conclusions based on the very low binding energies in the Prasongkit papers such as changes in conductance seem unrealistic. Thus, we have the strong suspicion that the binding site in the Prasongkit paper was not accurately optimized.*".

In the last paragraph, Grigoriev *et al.* wrote: "*The effect of the radical molecule, such as NO_2, on electron transport between two closely spaced gold electrode would be in introduction of electronic states close to Fermi level of metal electrodes, that would enable resonance tunneling between them. However, there is no mechanism that binds the gas molecule, neither is the size of NO_2 sufficient to bridge the gap in space between the electrodes, spaced to fit BPDT molecule in between.*".

The Comment attempted to criticize the electron transport mechanism of our published paper but not showing any

Division of Physics, Faculty of Science, Nakhon Phanom University, Nakhon Phanom 48000, Thailand. E-mail: jariyanee.prasongkit@npu.ac.th

information to support it. Contrary to what the Comment claims to have the strong adsorption energy, Grigoriev *et al.* have discussed about the van der Waals interactions: "*Introducing BPDT as a sensor we solve the problem of temporarily binding BPDT: 1 shows the charge density difference for NO_2 adsorption, that demonstrates clear, yet weak hydrogen bonding (blue deficiency blob around one of one of the 4 protons of the upper benzene ring of the molecule), while the body of the gas molecule is accommodated at the face of the lower ring with VdW interaction.*".

At the end of paragraph, the authors of the Comment wrote: "*In turn, this position of the gas introduces a sufficient distortion on the nearest benzene ring, which makes it possible for the metal-induced gap states (MIGS) induced from the gold to penetrate much further along BPDT, as can be seen on a LDOS plot nearby.*".

Grigoriev *et al.* have made some mistake in their DFT calculation, causing the distorted carbon ring structure and reactive to the NO_2. Consequently, it is unreliable when the authors of the Comment claimed that: "*Density of states, that would otherwise penetrate across sulfur and up to a first carbon atom in the ring, as seen on a top benzene ring, now resides on the whole lower ring, providing a conduction path for tunneling electrons. In other words, the real space span between the electrodes, that otherwise would be occupied by the MIGS in the HOMO–LUMO gap of the BPDT has now shrank by a half, facilitating electron tunneling at low bias.*".

Regarding the conduction path, the non-equilibrium Green's Function method[15,16] is required to describe it, however, the authors of the Comment just showed the LDOS plot from the DFT calculation that was not able to analyze the conduction channel.

Conflicts of interest

Prasongkit was a PhD student in Condensed Matter Theory group, at Uppsala University, Sweden and also was a member of the interdisciplinary center at Uppsala University, U3MEC (Uppsala University Unimolecular Electronics Centre) during 2006–2011. Prasongkit returned to Thailand and focused mainly on the theoretical studies of electron transport in nanosensor. In 2013, Prasongkit was a guest researcher on short-stays at Uppsala University and discussed the interaction between the BPDT and the gas molecules at the meeting.

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