ISSN 1742-6588

Journal of Physics
Conference Series

The 11th Biennial Conference on Classical and Quantum Relativistic Dynamics of Particles and Fields

1239

VOLUME 1239 – 2019

4–7 June 2018
Mérida, Yucatán, Mexico

EDITOR
Martin Land

The open access journal for conference proceedings

iopscience.org/jpcs

IOP Publishing

Journal of Physics: Conference Series

PAPER • **OPEN ACCESS**

Justification on cyclopropene to propyne isomerization pathway based on vibrational calculations

To cite this article: R Madinah *et al* 2020 *J. Phys.: Conf. Ser.* **1568** 012001

View the article online for updates and enhancements.

Journal of Physics: Conference Series **1568** (2020) 012001 doi:10.1088/1742-6596/1568/1/012001

Justification on cyclopropene to propyne isomerization pathway based on vibrational calculations

R Madinah[1], F Rusydi[1,2,*], L S P Boli[1], V Khoirunisa[1,3], M Z Fahmi[4] and A H Zaidan[1,2]

1 Research Center for Quantum Engineering Design, Faculty of Science and Technology, Universitas Airlangga, Jl. Mulyorejo, Surabaya 60115, Indonesia
2 Department of Physics, Faculty of Science and Technology, Universitas Airlangga, Jl. Mulyorejo, Surabaya 60115, Indonesia
3 Engineering Physics Study Program, Institut Teknologi Sumatera, Lampung 35365, Indonesia
4 Department of Chemistry, Faculty of Science and Technology, Universitas Airlangga, Jl. Mulyorejo, Surabaya 60115, Indonesia

*rusydi@fst.unair.ac.id

Abstract. We report a density-functional coupled with vibrational calculation on justifying the isomerization pathway of cyclopropene to propyne. The idea is to present the pathway in energy level diagram which the transition state is ensured by tracking a particular mode that supports the cyclic bond breaking and triple bond formation to occur. This mode decreases along the pathway and disappears at the transition state. To verify the designed pathway, the activation energy of the isomerization is used to find the rate constant with respect to experimental data at 500 K and 700 K by using transition state theory (TST). At those temperatures, TST predicts the rate constant at the same order of magnitude with the experimental result. It shows that the trend between calculation and experimental data is qualitatively in a good agreement, which implies that the designed pathway is justified. Furthermore, this study can be used as a guide if one needs to construct an isomerization pathway.

1. Introduction

An isomerization is the simplest chemical reaction. It involves only one molecule; hence, it is called a unimolecular reaction. Kinetically, it is a first-order reaction; consequently, the unit of its rate constant is 1/sec [1]. In most cases, isomerizations can occur in the gas phase and do not require a catalyst [2,3]. Even though it is simple, the mechanism of isomerization is not always straightforward. An isomerization commonly requires energy from the heat to begin. However, it not always the case, such as in isomerization of trans-HCOH to formaldehyde [4]. In this case, the isomerization occurs even without enough heat (at very low temperature, 11 K). The computational study revealed that the isomerization happens via quantum tunneling [5,6]. Therefore, experimental and computational studies are required to understand the isomerization mechanism.

One of the interesting isomerization to study computationally is cyclopropene to propyne. The reason is because this isomerization involves a C-C cyclic bond breaking and a C-C triple bond formation. The bond breaking and formation, in this case, hardly occur because of quantum tunneling, such as the case of trans-HCOH isomerization. Therefore, the isomerization is mostly due to the heat. Consequently,

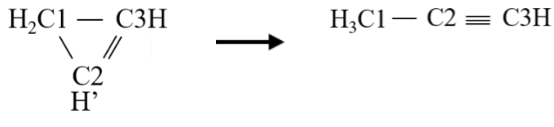
Journal of Physics: Conference Series **1568** (2020) 012001 doi:10.1088/1742-6596/1568/1/012001

there must be at least one vibrational mode that supports the bond breaking and formation to occur. Furthermore, this cyclopropene isomerization occurs in the gas phase and without catalyst [7]. It implies the isomerization is straightforward, but yet the mechanism is not necessarily simple.

2. Computational detail

2.1. Energy and structure calculations

We designed an isomerization pathway of cyclopropene to propyne as illustrated in the following scheme as shown in figure 1.



Cyclopropene Propyne

Figure 1. Initial and final states of cyclopropene isomerization in Kekule's structure.

We performed routine of ground state calculation [8] on initial and final structures. By tracking the vibrational mode, we predicted the transition state (TS) structure. For the TS structure, we applied TS optimization routine of calculation [8]. We constructed energy level diagram for all states based on density-functional calculations. We employed B3LYP as exchange-correlation functional and 6-311+G(d,p) as basis set that integrated in the Gaussian09 software.

2.2. Thermochemistry and chemical kinetics calculations

We calculated the standard enthalpy of reaction ($\Delta_r H°$) using the following formula,

$$\Delta_r H° = H°_{TS} - \Delta G°_{IS} \tag{1}$$

with IS and TS are the initial and the transition state, respectively. We calculated activation energy based on electronic energy (E_B), transition state theory (E_a) and Gibbs energy ($\Delta^{\ddagger} G°$) using the following formula [1]

$$E_B = E_{TS} - E_{IS} \tag{2}$$

$$E_a = \Delta^{\ddagger} H° + RT \tag{3}$$

$$\Delta^{\ddagger} G° = \Delta G°_{TS} - \Delta G°_{IS}. \tag{4}$$

We also calculated pre-exponential factor (A) using transition state theory as follows [1]:

$$A = \frac{e k_B T}{h c°} exp\left[-\frac{\Delta^{\ddagger} S°}{R}\right]. \tag{5}$$

The quantities in equation (1), (3), (4) and (5) are temperature dependence which calculated at room temperature. We performed the vibrational calculations at 500 K and 700 K to determine the rate constants which mathematically described as [1]

$$k(T) = \frac{k_B T}{h c°} exp\left[-\frac{\Delta^{\ddagger} G°}{RT}\right], \tag{6}$$

which k_B, h, R are the constant of Boltzman, Planck and molar gas. $c°$ is the molecule's concentration from the reactant to the transition state (which assume to be 1) [1], and T is the temperature. Then, we compared all these calculation results with experimental data to justify the designed pathway.

3. Results and discussion

3.1. Isomerization pathway design

Figure 2 shows the designed isomerization pathway of cyclopropene to propyne. The isomerization involves C-C cyclic bond breaking and a C-C triple bond formation. We design our pathway by displacing a hydrogen atom (labeled with H' in scheme 2, State A). The displaced H' to C1 causes the C-C cyclic bond between C1 and C3 is broken (State B). Then, the triple bond is formed (State C). Finally, the expected product in the final state is formed (State D).

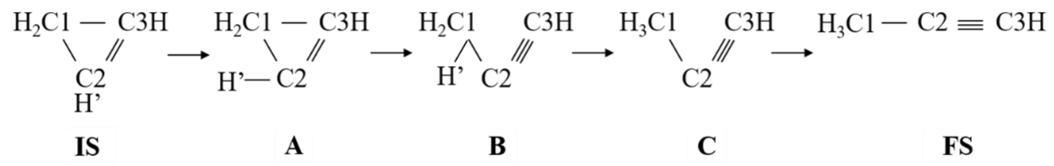


Figure 2. The designed isomerization pathway of cyclopropene to propyne.

3.2. Ground and transition states

Table 1 presents the geometrical parameters from DFT calculations (Calc.) and experiment (Expr.) [9]. Delta (Δ) in Table 1 is the discrepancy between our calculation results and the experimental value. The values of Δ in table 1 are within the accuracy limit according to Young [10]. It implies the selected exchange-correlation and basis set B3LYP/6-311+G(d,p) are suitable to study ground state of the molecules of interest.

Table 1. The selected geometrical parameters of cyclopropene (initial state) and propyne (final state) [9].

State		Bond Length				Bond Angle		
		C1-C2	C2-C3	C1-H	C3-H	C_1C_2H	C_1C_3H	HC_3H
Initial	Calc.	1.510	1.291	1.091	1.076	149.8		113.7
	Expr.	1.505	1.293	1.085	1.072	150.0		114.3
	Δ	0.005	-0.002	0.006	0.004	-0.2		-0.6
Final	Calc.	1.457	1.202	1.094	1.062		110.9	
	Expr.	1.459	1.206	1.105	1.056		110.2	
	Δ	-0.002	-0.004	-0.011	0.006		0.7	

Table 2 resumes the comparison between the initial state and state A, which are the value of relative energy, E_r; selected vibrational frequency, v_1; geometrical parameters: bond length (R) and bond angle (A). Energetically, the initial state is more stable than state A, which is as expected. The v_1 is the deduced as the one which triggers the isomerization as illustrated in figure 3.

Table 2. Some parameters of initial state and state A.

Parameter	Unit	IS	A
E_r	eV	0.00	1.50
v_1	1/s	781	-244
R C1-C2	Å	1.510	1.873
A C1C2H'	°	149.8	71.9
A C1C2C3	°	64.7	50.4

Journal of Physics: Conference Series **1568** (2020) 012001 doi:10.1088/1742-6596/1568/1/012001

The mode fulfills the requirement of our designed isomerization pathway (figure 2): the frequency decreases along the pathway and eventually becomes an imaginary number at state A. The imaginary frequency of State A indicates that structure in State A is close enough with the one in the transition state (TS). Therefore, the structure in State A is called as precursor geometry. The precursor geometry becomes our initial guess to do the TS optimization routine of calculation. Figure 4 illustrates the optimized TS geometry and the corresponding transition state.

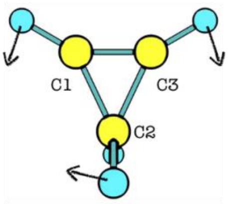


Figure 3. The illustration motion of selected vibrational v_1 of cyclopropene.

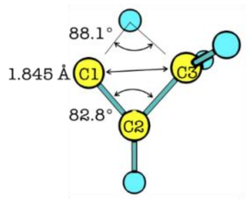
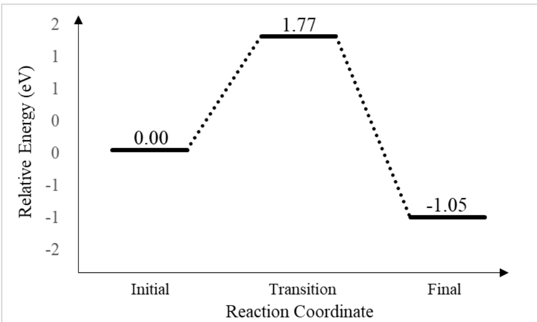


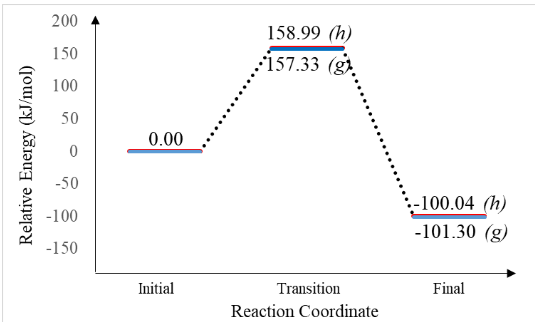
Figure 4. Optimized geometrical structure of transition state with $v_1 = -927$ 1/s.

3.3. Energy level diagram

Figure 5a and b show the energy level diagram (ELD) of the isomerization. Figure 5a is based on electronic energy, while figure 5b is after thermal corrections: enthalpy and Gibbs free energy. These ELDs give us three interesting facts: First, thermal corrections do not change the trend of ELD (there is one transition state which indicates a one-step reaction mechanism). Second, the negative value of $\Delta_r H°$ indicates an exothermic reaction, which agrees with an experimental fact (expr. = 92.2kJ/mol) [6]. Third, the comparison between E_B, TST (E_a), and $\Delta^{\ddagger} G°$, with experimental data ($E_{a\,\mathrm{expr.}}$ =147 kJ/mol) shows that $\Delta^{\ddagger} G°$ gives the most accurate prediction to the activation energy.



(a)



(b)

Figure 5. Energy level diagrams of the isomerization (a) based on electronic energy and (b) after thermal correction at room temperature (298.15K). The red and blue line in Figure 5(b) is for enthalpy (labeled with *h*) and Gibbs free energy (labeled with *g*), respectively. The value of $\Delta^{\ddagger} H°$ plus RT factor is 161 kJ/mol (the activation energy, E_a based on TST).

3.4. Chemical kinetics quantities

Table 3 presented the kinetic quantities based on TST and experimental results [1]. The Δ is the discrepancy between our calculation results and the experimental value. The value of Δ shows that calculation based on TST gives a value that agrees with the experiment. However, the calculation does not give a good prediction for the natural logarithmic of the pre-exponential factor, *ln*(A). The prediction of A depends on the vibrational frequency: the higher bond order of C-C, the higher the error of the calculated C-C vibrational frequency [11]. In this case, the isomerization involves single C-C cyclic bond breaking and C-C triple bond formation. Therefore, the error in the vibrational frequency calculations of the isomerization leads to error in the calculated *ln*(A).

Table 3. The values of Arrhenius parameter and rate constant from TST (Calc.) and experiment (Expr.) [1].

Reac. Quantities	Unit	Expr.	Calc.	Δ
E_a	kJ/mol	147	161	14
$ln(A)$	1/s	27.9	30.7	2.8
k(500K)	1/s	5.67E-04	6.98E-04	same order
k(700K)	1/s	1.35E+01	4.49E+01	same order

Table 3 shows that the calculated rate constants are in the same order of magnitude with the experimental data. It indicates that the obtained TS geometry, and consequently our designed isomerization pathways (scheme 2) are correct. Also, ν_1 is the vibrational frequency that initiates the isomerization. Accordingly, we have successfully explained the mechanism of isomerization via vibrational movement. Furthermore, this study can be used as a guide if one needs to construct an isomerization pathway.

4. Conclusion

We have successfully justified the constructed isomerization pathway of cyclopropene to propyne based on vibrational calculations. We calculated activation energy in terms of E_B, E_a (based on TST), and $\Delta^{\ddagger}G°$, with $\Delta^{\ddagger}G°$ as the most accurate one. Furthermore, the comparison between the calculated rate constants is in the same order of magnitude with experimental data ($\sim 10^{-4}$ 1/s at 500 K and $\sim 10^{1}$ 1/s at 700 K). It implies that the constructed pathway is the correct mechanism of cyclopropene to propyne isomerization. Finally, this study can be used as a guide if one needs to construct an isomerization pathway based on vibrational calculation.

Acknowledgements
The authors thank to Rizka Nur Fadilla and Nufida Dwi Aisyah (Research Center for Quantum Engineering Design, Universitas Airlangga, Indonesia) for their insight and valuable discussions. This research is funded by Research and Innovation Institute, Universitas Airlangga through Riset Kolaborasi Mitra Luar Negeri Universitas Airlangga 2019.

References

[1] McQuarrie D A and Simon J D 1997 *Physical Chemistry: A Molecular Approach* (California: University Science Books)
[2] Kumaran S S, Lim K P, Michael J V, Tilson J L, Suslensky A and Lifshitz A 1996 *Isr J Chem* **36** 223
[3] Schneider F W and Rabinovitch B S 1962 *J Am Chem Soc* **84** 4215
[4] Schreiner P R, Resienauer H P, Pickard F C IV, Simmonett A C, Allen W D, Mátyus E and Császár A G 2008 *Nature* **453** 906
[5] Fadilla R N, Aisyah N D, Dipojono H K and Rusydi F 2017 *Procedia Eng.* **170** 113
[6] Aisyah N D, Fadilla R N, Dipojono H K and Rusydi F 2017 *Procedia Eng.* **170** 119
[7] Karni M, Oref I, Barzilai-Gilboa S and Lifshitz A 1988 *J Phys Chem A* **92**(24) 69249
[8] Foresman J B and Frisch A 1995-96 *Exploring Chemistry with Electronic Structure Methods* (Pittsburgh PA: Gaussian Inc.)
[9] Haynes W M 2015 *CRC Handbook of Chemistry and Physics* (California: CRS Press)
[10] Young D C 2001 *Computational Chemistry: A Practical Guide for Applying Techniques to Real-World Problems* (Third Avenue, New York: John Wiley & Sons)
[11] Jaramillo J and Scuseria G E 1999 *Chem Phys Lett* **312** 269

PAPER • OPEN ACCESS

Editorial Board

To cite this article: 2017 *J. Phys.: Conf. Ser.* **817** 011002

Editorial Board

Eni Sugiarti (eni.sugiarti@lipi.go.id)
Indonesian Institute of Sciences (LIPI)
Research Center for Physics
Komplek PUSPIPTEK Serpong,
Tangerang Selatan 15314,
Indonesia

Titi Anggono (titi.anggono@lipi.go.id)
Indonesian Institute of Sciences (LIPI)
Research Center for Physics
Komplek PUSPIPTEK Serpong,
Tangerang Selatan 15314,
Indonesia

Isnaeni (isnaeni@lipi.go.id)
Indonesian Institute of Sciences (LIPI)
Research Center for Physics
Komplek PUSPIPTEK Serpong,
Tangerang Selatan 15314,
Indonesia

Yuliati Herbani (yuliati.herbani@lipi.go.id)
Indonesian Institute of Sciences (LIPI)
Research Center for Physics
Komplek PUSPIPTEK Serpong,
Tangerang Selatan 15314,
Indonesia

Ferensa Oemry (ferensa.oemry@lipi.go.id)
Indonesian Institute of Sciences (LIPI)
Research Center for Physics
Komplek PUSPIPTEK Serpong,
Tangerang Selatan 15314,
Indonesia

Hubby Izzuddin (hubby.izzuddin@lipi.go.id)
Indonesian Institute of Sciences (LIPI)
Research Center for Physics
Komplek PUSPIPTEK Serpong,
Tangerang Selatan 15314,
Indonesia

Widi Astuti (widi.astuti@lipi.go.id)
Indonesian Institute of Sciences (LIPI)
Research and Development Division for Mineral Technology
Jl. Ir Sutami Km.15 Tanjung Bintang, Lampung Selatan
Lampung. 35361
Indonesia

Wahyu Bambang Widayatno (wahyu.bambang.widayatno@lipi.go.id)
Indonesian Institute of Sciences (LIPI)

Research Center for Physics
Komplek PUSPIPTEK Serpong,
Tangerang Selatan 15314,
Indonesia

Deni Shidqi Khaerudini (deni.shidqi.khaerudini@lipi.go.id)
Indonesian Institute of Sciences (LIPI)
Research Center for Physics
Komplek PUSPIPTEK Serpong,
Tangerang Selatan 15314,
Indonesia

Kirana Yuniati Putri (kirana.yuniati.putri@lipi.go.id)
Indonesian Institute of Sciences (LIPI)
Research Center for Physics
Komplek PUSPIPTEK Serpong,
Tangerang Selatan 15314,
Indonesia

Fredina Destyorini (fredina.destyorini@lipi.go.id)
Indonesian Institute of Sciences (LIPI)
Research Center for Physics
Komplek PUSPIPTEK Serpong,
Tangerang Selatan 15314,
Indonesia

Nurfina Yudasari (nurfina.yudasari@lipi.go.id)
Indonesian Institute of Sciences (LIPI)
Research Center for Physics
Komplek PUSPIPTEK Serpong,
Tangerang Selatan 15314,
Indonesia

Qolby Sabrina (qolby.sabrina@lipi.go.id)
Indonesian Institute of Sciences (LIPI)
Research Center for Physics
Komplek PUSPIPTEK Serpong,
Tangerang Selatan 15314,
Indonesia

Risma Sundawa (risma.sundawa@gmail.com)
Indonesian Institute of Sciences (LIPI)
Research Center for Physics
Komplek PUSPIPTEK Serpong,
Tangerang Selatan 15314,
Indonesia

Journal of Physics: Conference Series

COUNTRY	SUBJECT AREA AND CATEGORY	PUBLISHER	H-INDEX
United Kingdom Universities and research institutions in United Kingdom	Physics and Astronomy Physics and Astronomy (miscellaneous)	IOP Publishing Ltd.	70

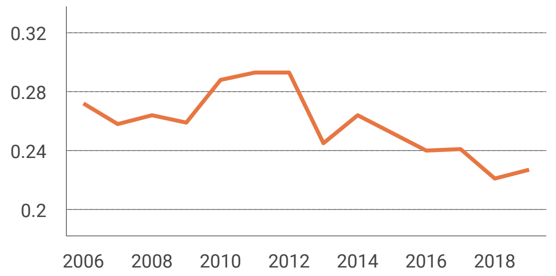
PUBLICATION TYPE	ISSN	COVERAGE	INFORMATION
Conferences and Proceedings	17426588, 17426596	2005-2020	Homepage How to publish in this journal jpcs@ioppublishing.org

SCOPE

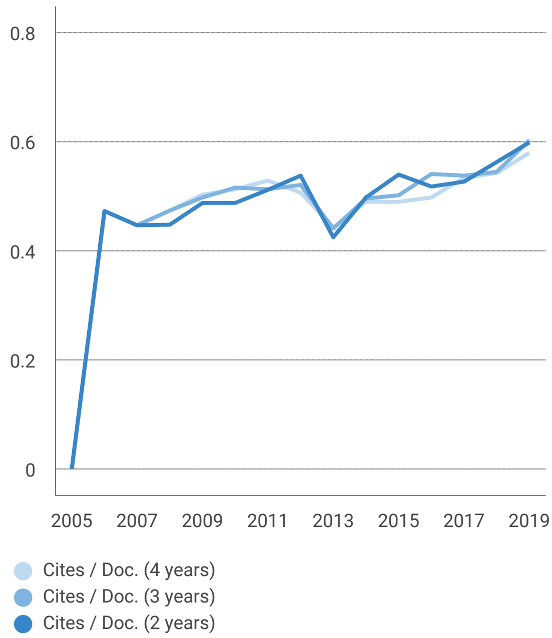
The open access Journal of Physics: Conference Series (JPCS) provides a fast, versatile and cost-effective proceedings publication service.

Join the conversation about this journal

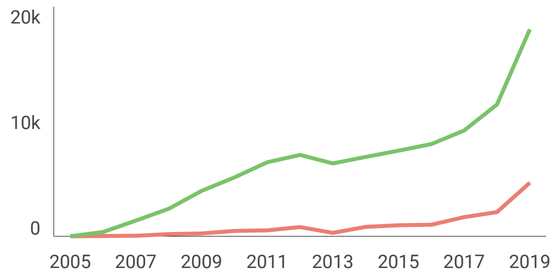
SJR



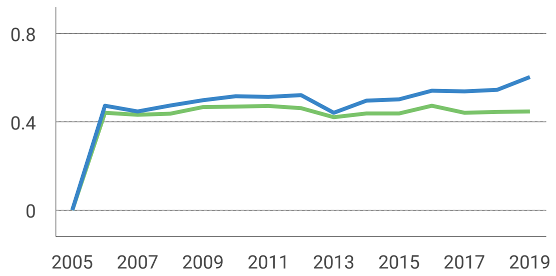
Citations per document



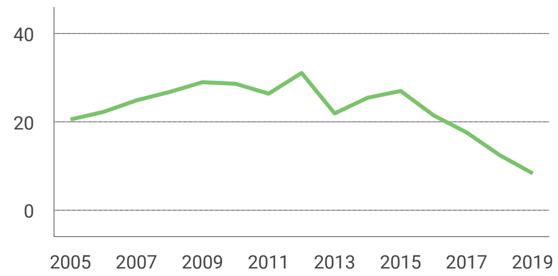
Total Cites Self-Cites



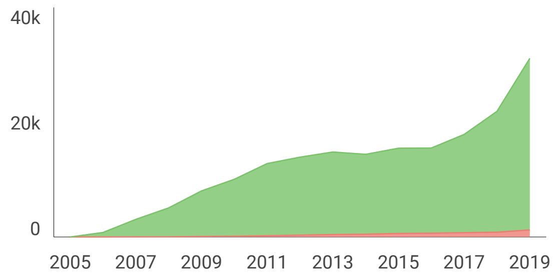
External Cites per Doc Cites per Doc



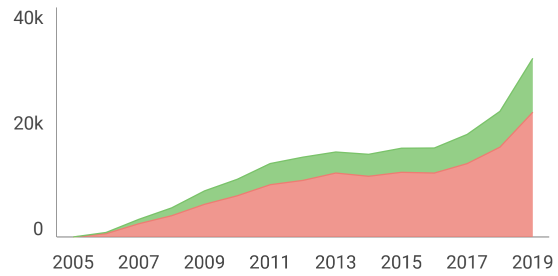
% International Collaboration

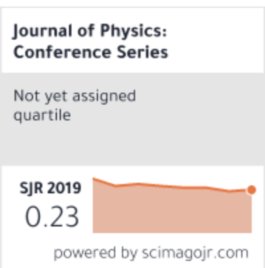


Citable documents Non-citable documents



Cited documents Uncited documents





← Show this widget in your own website

Just copy the code below and paste within your html code:

<a href="https://www.scimag

Metrics based on Scopus® data as of April 2020

Table of contents

Volume 1568

2020

Previous issue   Next issue

4th-Padjadjaran International Physics Symposium 2019 (4th-PIPS-2019) 13-14 November 2019, Bandung, West Jawa, Indonesia

Accepted papers received: 22 May 2020
Published online: 03 July 2020

Open all abstracts

Preface

Computational and Modelling

Instrumentation and Electronics

Energy

Biophysics

Geophysics

JOURNAL LINKS