



**PROVIDENCE WOMEN'S COLLEGE**

**COLLEGE WITH POTENTIAL FOR EXCELLENCE**

**Re-Accredited with grade A<sup>+</sup> by NAAC**

---

## **CRITERIA 3- RESEARCH INNOVATIONS AND EXTENSION**

### **Key Indicator 3.3- Research Publication and Awards**

**3.3.2: Number of books and chapters in edited volumes/books published and papers published in national/international conference proceedings per teacher during last five years.**

The Book review genre: Biological Studies of Vegetable mite on Moringa oleifera Lam focuses on unveling the biology and life table parameters of a minute, microscopic and highly invasive vegetable mite, Tetranychus neocaledonicus Andre on a previously unrecorded host Moringa oleifera Lam. Moringa is a plant having nutritional, medicinal and veterinary significance. Owing to the cryptic behaviour of the vegetable mites, they tend to remain unnoticed by the farmers in the field. The loss would count in tune beyond comparison by the time the mite is spotted on the host. The mites have piercing and sucking type of mouth parts with which it removes the plant sap leading to chlorosis, necrosis, wilting and finally branch die back of the host. This has to be considered seriously in a state like Kerala where more than half of the population depend on agriculture for their livelihood. The current investigation has led to the unveiling of a new host, previously unrecorded so far.



Sangeetha Kaimal

## Breeding Biology of the Vegetable Mite on Moringa oleifera Lam



Dr Sangeetha G Kaimal is currently working as Assistant Professor in Zoology, Providence Women's College, Calicut, Kerala, India. She did her Ph.D and M.Phil in Zoology with Acarology as her specialisation. She has authored around 20 papers in National and International Journals. As an acarologist, her area of interest include that of Spider Mites.



978-3-659-78830-7

 **LAMBERT**  
Academic Publishing

**Imprint**

Any brand names and product names mentioned in this book are subject to trademark, brand or patent protection and are trademarks or registered trademarks of their respective holders. The use of brand names, product names, common names, trade names, product descriptions etc. even without a particular marking in this work is in no way to be construed to mean that such names may be regarded as unrestricted in respect of trademark and brand protection legislation and could thus be used by anyone.

Cover image: [www.ingimage.com](http://www.ingimage.com)

Publisher:

LAP LAMBERT Academic Publishing

is a trademark of

International Book Market Service Ltd., member of OmniScriptum Publishing Group

17 Meldrum Street, Beau Bassin 71504, Mauritius

Printed at: see last page

ISBN: 978-3-659-78830-7

Zugl. / Approved by: Calicut, University of Calicut, 2006

Copyright © Sangeetha Kaimal

Copyright © 2019 International Book Market Service Ltd., member of  
OmniScriptum Publishing Group



# Biota.

A Compendium of  
Research papers

Editors:

Abhilash E.S. | Thejass P. | Sinitha K.



UGC – HUMAN RESOURCE DEVELOPMENT CENTRE  
UNIVERSITY OF CALICUT



UGC – HUMAN RESOURCE DEVELOPMENT CENTRE  
UNIVERSITY OF CALICUT

# Biota - A Compendium of Research papers

Editors:

Dr. Abhilash E.S.

Dr. Thejass P.

Dr. Sinitha K.



Nadakkavu, Kozhikode, Kerala

Tel:0495-4020666

[www.insightpublica.com](http://www.insightpublica.com)|[www.bookat.in](http://www.bookat.in)

e-mail: [insightpublica@gmail.com](mailto:insightpublica@gmail.com)

**BIOTA - A COMPENDIUM OF RESEARCH PAPERS**

Editors: **Dr. Abhilash E.S., Dr. Thejass P., Dr. Sinitha K.**

ISBN 978-93-89155-16-7

Published in April 2019

Copyright©Reserved

All Rights reserved. No Part of this Publication may be reproduced, stored in a retrieval system, or transmitted, in any form, or by any means, electronic, mechanical, photocopying, recording or otherwise, without the prior permission of the publisher.

Cover Design: KJ VJ

Published by

Publication: UGC-Human Resource Development Centre

University of Calicut

Insightinpublica Printers & Publishers Ltd.

Printed and bounded in India by

Manipal Technologies Limited, Manipal

₹ 400



17- Life Science Research... university of Calicut is acknowledged for his constant encouragement and technical support provided to publish this book.

Indeed this is a great achievement of our teachers despite their hectic academic time schedule. We appreciate their endeavor

Lastly, this is a humble initiative from our side, and kindly bear with us, if any mistake overseen has got in without our knowledge.

**Dr. Abhilash.E.S, Dr. Thejass.P and Dr. Sinitha.K**  
*Editors of the book*

## Contents

- Plant ecological studies on the moist deciduous forests of Godrichal reserve forest; Southern Western Ghats of India.  
*Abhilash E.S.* 9
- Variability in rice diet among ethnic population around Palakkad City *Dr. K.Abdul Rasheed* 14
- Vascular epiphytic plants on a tropical rain forest tree *Elaeocarpus tuberculatus* Roxb in Silent Valley National Park, The Western Ghats, India. *K.S. Anoop Das, V.S. Ramachandran Lalitha Vijayan* 19
- Birds of Kottathalachi Mount, Western Ghats, Kannur, Kerala, *Haritha T Nair, Sarangi, N.V. and Sneha, C.* 28
- Algal mediated biosynthesis of silver nanoparticles using *Gracilaria textorii* (Suring.) J.ag. (Red seaweed) and evaluation of their antibacterial activity *John Peter Paul, J. Iniya Udhaya, C* 33
- Breeding Biology of *Protoribates punctata* on Highly Recalcitrant Coconut Pith *Julie E and Ramani N* 51 - 56
- Analysis of the Presence of Bioactive Compounds during the Process of Germination of *Phaseolus aureus* Seeds *Kavitha. O* 57
- Documentation of the Alien Invasive Species in and around the Government College Kasaragod, Kasaragod *Maju T. T., Biju P and Krishnakumar K.A.* 63
- Study on Nomiinid Bees (Apiformes; Halictidae) of Kerala *Manjusha K.T. and Jobiraj T.* 71

# Breeding Biology of *Protoribates punctata* on Highly Recalcitrant Coconut Pith

**Julie E**

Assistant Professor, Department of Zoology,  
Providence Women's College, Calicut  
julie.ajai@gmail.com (Corresponding Author)

**Ramani N**

Professor, Department of Zoology,  
University of Calicut

## Abstract

In the present study, assessment of the reproductive potential of panphytophagous mites *Protoribates punctata* on highly recalcitrant materials like coconut pith, left behind after coir retting process was made. The study site was a regular retting ground bordered by trees like *Cocos nucifera*, *Avicennia officinalis* and *Acanthus ilicifolius*. Collected samples were subjected to extraction under a modified Berlese-Tullgren funnel apparatus in the laboratory. Live mites for biological studies were extracted into collecting vials containing water/moistened pith. The pith was found consumed by the adults larva and the nymphs of *P.punctata*. Under laboratory conditions at 30°C and 70% RH, *P. punctata* completed its development from egg to adult within 29.5 -34 days.

**Keywords:** Panphytophagous mites, Oribatid mites, Panphytophagy.

## Introduction

Oribatid mites exhibit a wide variety of nutritional habits (Haq and Prabhoo, 1976). This imposes selection in pattern of their distribution, each species being better adapted to specific habitat which will offer their preferred food in plenty. The diverse feeding trends and wide distribution pattern of these mites helped to consider them as a panphytophagous group (Haq, 1996). Panphytophagy represents a feeding category which is determined by the possession of a combination of several characters of morphological and physiological significance. Possession of this type of diverse feeding trends helps them to explore more habitats to enjoy wider distribution as noted earlier (Behan and Hill, 1978; Haq, 2001). In the present study, assessment of the reproductive potential of panphytophagous mites *Protoribates punctata* on highly recalcitrant materials like coconut pith, left behind after coir retting process was made.

## Materials and Methods

The site selected was Feroke, a census town known as the "cradle of the tile industry" in Kerala and located at 11° 11' 01.38"N, 75° 50' 54.10"E. The study site was a regular retting ground bordered by trees like *Coco snucifera*, *Avicennia officinalis* and *Acanthus ilicifolius*. Collected samples were subjected to extraction under a modified Berlese-Tullgren funnel apparatus in the laboratory. Live mites for biological studies were extracted into collecting vials containing water/moistened pith. The process of extraction was carried out for a period of 2-3 days depending upon the moisture content of the samples. Live mites were picked up with a moistened camel hair brush under a stereomicroscope and transferred in to individual culture cells for subsequent rearing. Rearing of selected species of oribatid mites was carried out in the laboratory in plastic chambers based with plaster of Paris- charcoal mixture (4:1). Fresh coconut pith collected from the retting grounds were kept in polythene bags and brought to the laboratory. This was dried in an oven at 103°C for 1-2 days and stored in desiccators for subsequent use as test food item. Food item was offered individually at the center of the culture cell. Regular observation was made regularly thrice a day.

## Results and Discussion

Coconut pith has a very high water holding capacity and is very stable because of the presence of high percentage of lignin which takes decades to decompose. The pith was found consumed by the adults larva and the nymphs of *P.punctata*. (Julie and Ramani, 2007). *Protoribates*, in general comprises very active forms with a wide range of tolerance to various environmental factors (Julie and Ramani, 2015). Laboratory feeding experiments carried out on *P. punctata* revealed this species as a voracious feeder of coir pith on which it could successfully complete several generations. This species also was recognized as a bisexual species in both field and laboratory conditions. Postembryonic development of *P. punctatus* also initiated with the deposition of spermatophores by males. The deposition of spermatophores in oribatid mites was reported in a number of species by various authors (Shereef, 1977; Julie and Ramani, 2009). Males laid innumerable number of spermatophores singly on and around the food items, 5-8 days after their emergence. The spermatophores of *P. punctatus* appeared as dew drops, unstalked, bearing globular shining heads. The spermatophore head measured 46- 51  $\mu\text{m}$  in length and 35-38  $\mu\text{m}$  in width. Stalk of spermatophores measured 69-73  $\mu\text{m}$ . A single male laid 15-25 spermatophores per day. Spermatophore deposition lasted for 25-30 days. The females wandered inside the culture cells with their genital flaps widely opened so as to take up the globular heads of the spermatophores through the genital opening. Several such deheaded spermatophore stalks could be observed in the culture cells/walls of culture cells. The females which actively took up spermatophores started oviposition after 8-9 days. Concealed places in culture chambers were the preferred sites for oviposition. Freshly laid eggs appeared oval in shape and translucent. The incubation period lasted for 5-6 days. As the incubation period progressed, there appeared an area of weakness at the anterior pole, which developed into a slit and got extended in either direction laterally to the posterior pole. Prior to this observation, the egg got changed to reddish to pale brown in colour. The egg case lastly cleaved in to two halves, leading to the emergence of a hexapod larva. The larva appeared highly lethargic soon after hatching and initially it showed sluggish movement and resumed normal activities and feeding after 10-20 minutes. The active feeding period of the larva lasted

for 2-3 days. At the end of its active feeding period, gradually it became swollen in appearance, sluggish in habit and stopped feeding. This inactive phase was recognized as the first quiescent phase. The duration of the quiescent phase was the same as that of the active period. The end of quiescence was marked by the moulting process which lasted for 2 hours. Moulting of the larva was found completed following the same pattern and it was found initiated by the development of a posterolateral slit on either side of the notogaster and each slit gradually extended to meet medially. After about 45 minutes, the prodorsum of the emerging nymph was found protruded through the slit, as a consequence of its wriggling movements. Progressive up and down movements of moulting instar resulted in the lifting off of the dorsal half of the exuvium and the release of protonymph, leaving behind the exuvium. The protonymph emerged was slightly larger than the larva and was an octapod. Newly moulted nymph remained stationary for 15-25 minutes near the exuvium and initiated wandering in search of food. On reaching the food item i.e., the coconut pith, the protonymph started feeding. The active period of the protonymph lasted for 3-4 days and then it entered in to second quiescent phase of 2.25-3.00 days duration. Subsequent moulting of protonymph led to the emergence of the deutonymph which was larger than the previous stage. The feeding period of the deutonymph lasted for 3 to 5 days, and after which it passed through a quiescent phase of 3-4 days duration. On subsequent moulting of the III<sup>rd</sup> quiescent phase, the tritonymph emerged, which was the largest among the juveniles. Tritonymph was creamy yellow in colour with brown legs and was observed to feed voraciously on the pith for 4-6 days. On the 3<sup>rd</sup> or 4<sup>th</sup> day of its quiescent phase, the colour of the nymph got changed to light brown. Subsequent to this colour change, moulting of the tritonymph took place and the adult emerged. The newly emerged adult was less sclerotized. Within 2-3 days of emergence, the colour of the body of the adult got changed into dark brown. The intense feeding activity of oribatid mites on the pith helped to fragment the pith into single fibers and heaps of faecal pellets. Continued feeding activity of the immatures and the adults of this species confining them to the pith resulted in the formation of small cavities, burrows and holes filled with faecal pellets, eggs and immatures. Generally, the feeding efficacy of the immature stages of oribatid

mites is comparatively greater than that of the adults (Haq and Ramani, 1984). The nymphal stages of the species studied were proved highly voracious feeders on their respective favourable items of food given. This suggests that the role of immatures in the turnover of nutrients is comparatively greater than that of the adult mites.

## Conclusion

Under laboratory conditions at 30°C and 70% RH, *P. punctata* completed its development from egg to adult within 29.5 -34 days on highly recalcitrant material like coconut pith.. The newly emerged males started deposition of spermatophores within 4-6 days and the newly emerged females initiated oviposition after 8-9 days of active feeding on pith. Thus, the F<sub>1</sub> generation was completed within 37.5-43 days.

## References

- Behan- Pelletier, V.M. and Hill, S.B. 1978. Feeding habits and spore dispersal of oribatid mites in the North American arctic. *Revue-d'Ecologie- et-de-Biologie-du-sol*. 15(4): 497-516.
- Haq, M.A. 1996. Nutritional diversity of oribatid mites in relation to soil fertility. *J. Karnataka Univeristy, Science Special Issue*, 76-91.
- Haq, M.A. 2001. Oribatidmites strategies in relation to environment. *Entomon.*,26: 305-309.
- Haq, M.A. and Prabhoo, N.R. 1976. Observations on the feeding habits of Oribatid mites from the soils of Kerala (Acarina: Gyptostigmata)-Panphytophages. *Entomon*, 1(2): 133-137.
- Haq, M.A. and Ramani, N. 1984. Post Embryonic development of *Paramellobatesbengalensis* (Acari: oribatei) parasitic on *Dioscoriaalata*. In: D.A. Griffiths and C.E. Bowman (Eds.) *Acarology VI*, 2 Ellis Hopwood Ltd. Chichester, England. 819-825.
- Julie, E. and Ramani, N.2007. Role of oribatid mites in the degradation highly recalcitrant solid wastes on retting grounds. *J. Acarol*. 27-28.
- Julie, E. and Ramani, N.2009. Studies on spermatophore depo-

ഡോ. എസ് ശ്രീകുമാരി



കേരളീയ  
സ്ത്രീനവോത്ഥാന  
ചരിത്രം



keraleeya stree navodhana charithram

•  
dr. s sreekumari

•  
first edition  
january 2019

•  
published  
chintha publishers, thiruvananthapuram

•  
typesetting  
star communications, thiruvananthapuram

•  
printed  
akshara offset, thiruvananthapuram

•  
cover  
vinod

•  
price  
rupees two hundred and forty only

Rights reserved

---

**വിതരണം**

ദേശാഭിമാനി ബുക്ക് ഹൗസ്  
H O തിരുവനന്തപുരം-695 035  
phone: 0471-2303026, 6063026  
www.chinthapublishers.com  
chinthapublishers@gmail.com

**ബ്രോഞ്ചുകൾ**

ഹെസ്റ്റാഫീസ് ബ്രോഞ്ച് കുന്നുകുഴി • സ്റ്റാച്യു തിരുവനന്തപുരം • കെ എസ് ആർ ടി സി ബസ് സ്റ്റേഷൻ ആലപ്പുഴ • കെ എസ് ആർ ടി സി ബസ് സ്റ്റേഷൻ എറണാകുളം • മച്ചിങ്ങൽ ലെയ്ൻ തൃശ്ശൂർ • ഐ ജി റോഡ് കോഴിക്കോട് • മാവൂർ റോഡ് കോഴിക്കോട് • എൻ ജി ഒ യൂണിയൻ ബിൽഡിംഗ് കണ്ണൂർ • സെൻട്രൽ ബസ് ടെർമിനൽ കോംപ്ലക്സ് താവക്കര കണ്ണൂർ

---

CO - 2743 / 4937  
ISBN - 978-93-88485-16-6



# കേരളീയ സ്ത്രീനവോത്ഥാന ചരിത്രം

ഡോ. എസ് ശ്രീകുമാരി

കേരളത്തിലെ നവോത്ഥാന കാലത്തിനു മുൻപ് സമൂഹത്തിൽ സ്ത്രീക്കുള്ള സ്ഥാനവും ജാതി വ്യവസ്ഥയും അനാചാരങ്ങളും കൊണ്ട് ഇരുണ്ടു പോയ കാലത്തെ സ്ത്രീയുടെ അവസ്ഥയും, നവോത്ഥാനകാലത്തെ മാറ്റങ്ങളുമാണ് ഈ പുസ്തകത്തിൽ പ്രധാനമായും പരിശോധിക്കുന്നത്. സമകാലിക കേരളീയ വനിതയുടെ അനുഭവങ്ങളും സ്ത്രീ സ്വതന്ത്രപീഠങ്ങളുടെ പ്രശ്നങ്ങളും സ്ത്രീ സംഘടനകളുടെ ആവിർഭാവവും സ്ത്രീസുരക്ഷയുടെയും പ്രശ്നങ്ങളും ഇതിൽ ചർച്ച ചെയ്യുന്നുണ്ട്.

ISBN 93-88485-16-5



വില: ₹ 240

  
ചിന്ത പബ്ലിഷേഴ്സ്  
തിരുവനന്തപുരം

# histories unbounded

SELECTED PAPERS OF  
THIRD KERALA HISTORY CONGRESS

GENERAL EDITOR  
T MUHAMMEDALI



# HISTORIES UNBOUNDED

General Editor  
T. Muhammedali



**Kerala History Congress**

 **Current Books**

ENGLISH & MALAYALAM LANGUAGES  
Histories Unbounded

HISTORY  
General Editor T. Muhammedali

Rights Reserved  
First Published May 2019

PUBLISHERS  
Current Books  
An imprint of D C Books  
Kerala State, India  
Literature News Portal: [www.dcbooks.com](http://www.dcbooks.com)  
Online Bookstore: [www.onlinestore.dcbooks.com](http://www.onlinestore.dcbooks.com)  
e-bookstore: [ebooks.dcbooks.com](http://ebooks.dcbooks.com)  
Customercare: [customercare@dcbooks.com](mailto:customercare@dcbooks.com), 9846133336

DISTRIBUTORS  
DC Books-Current Books  
INDIA

D C BOOKS LIBRARY CATALOGUING IN PUBLICATION DATA  
Histories unbounded

752p., 21cm.

ISBN 978-93-5282-747-3.

Editor: T. Muhammedali.

1. History. I. Muhammedali, T.

954-dc 22

No part of this publication may be reproduced, or transmitted in any form  
or by any means, without prior written permission of the publisher.

ISBN 978-93-5282-747-3

Printed in India  
at Manipal Technologies, Limited, Manipal

CURRENT BOOKS - THE FIRST INDIAN BOOK PUBLISHING HOUSE TO GET ISO CERTIFICATION

206/19-10-Sl.No. 19059-dcb 7182-300(POD)-56828-05-19-p as

Port Cities, Bazaars, and 'Frontier Regimes' The Political Economy of Malabar (c. 1500-1800) <i>Dr. Binu M. John</i> .....	255
Social Reformers and Kerala Historiography: A Preliminary Reading of the Pracheena Malayalam of Chattampi Swamikal <i>T. Muhammedali</i> .....	279
Brothers at Our Door : The Unapplauded Role of Migrant Labour in Transforming Kozhikode <i>Dr. Priyadarsini P</i> .....	287
Bazaar Walks: Exploring the Spatial Transformations of Trade in Broadway, Ernakulam <i>Binu K. T</i> .....	300
Dalit as Margin Body: Re-reading Untouchability and Exclusionary process <i>Rajesh Komath</i> .....	308
Swami Ananda Theerthan: A Revolutionary Social Reformer of North Malabar <i>Dr. G. Premkumar</i> .....	320
Gender, Medicine and Modernity; Medicalization of the Female Body in Late Nineteenth Century Travancore <i>Anulekshmi U. G.</i> .....	336
Gods in Markets: Phantasmagorias and the Politics of God Images in Indian Advertisements <i>Arun M</i> .....	344

## **Brothers at Our Door : The Unapplauded Role of Migrant Labour in Transforming Kozhikode**

Dr. Priyadarsini P\*

Human migration that has been there from time immemorial continues even today and its repercussions are all pervasive. Globalization a relatively new phenomenon has increased the demand for workers from other countries in order to sustain national economies. Known as "economic migrants," these individuals are generally from impoverished developing countries migrating to obtain sufficient income for survival. This income is usually sent home to family members in the form of remittances and has become an economic staple in a number of developing countries. People also move or are forced to move as a result of conflict, human rights violations, violence, or to escape persecution. Another reason people move is to gain access to opportunities and services or to escape extreme weather. This type of movement is usually from rural to urban areas and is known as internal migration. Socio-cultural and geo-historical factors also play a major role. It is very common amongst people in African countries to migrate to the west as a matter of prestige.

This paper focuses on labour migration to Kerala from North Indian states like West Bengal, Jharkhand, Orissa, Chattisgarh and also from the North Eastern Indian states which is the result of wage difference between these geographic locations. The wage differences are usually linked to geographic labor demand and supply. It can be said that areas with a shortage of labor but an excess of capital have a high relative wage while areas with a high labor supply and a dearth of capital have a low relative wage. Labor tends to flow from low-wage areas to high-wage areas. Often, with this flow of labor bring about changes in the sending as well as the receiving destination. Kerala which is considered as India's Gulf in the north Indian rural villages has been one of the most liked destinations by the labourers for the past few decades.

\* Assistant Professor, Providence Women's College, Kozhikode -9



ഡോ: എസ്. ശ്രീകുമാരി

# മാറുന്ന കാലം മാറുന്ന സ്ത്രീജീവിതം



malayalam language  
marunna kalam  
marunna sthree jeevitham  
by: dr. s. sreekumari

first progress edition: mar 2019  
© rights reserved

cover & typesetting:  
progress graphics & designs  
printing: printout villa, mukkam.

publishers:  
Progress Publication,  
Room No: E-3, O.M. Building,  
Makkolath Road,  
Opp. Coronation Theatre, Calicut - 4  
progresspublication@gmail.com  
Ph: 0495 4019650,  
9995368733

notice: no part of this publication may be reproduced or  
transmitted in any form or by any means without  
prior written permission of the publisher.

UGC, CPE ഫണ്ട് ഉപയോഗിച്ച് പ്രസിദ്ധീകരിക്കുന്നത്

isbn: 978-93-84638-19-1  
₹. 130

# മാറുന്നകാലം മാറുന്ന സ്ത്രീജീവിതം

ഡോ: എസ് ശ്രീകുമാരി

പ്രോഗ്രസ് ബുക്സ്  
കോഴിക്കോട്- 4



**മാറുന്നകാലം മാറുന്ന സ്ത്രീജീവിതം**

**ഡോ: എസ്. ശ്രീകുമാരി**

ആധുനിക കേരളനിർമ്മിതിയുടെ ചരിത്രത്തിലെ സ്ത്രീ മുന്നേറ്റങ്ങളെ രേഖപ്പെടുത്തുന്ന ഗവേഷണപഠനങ്ങളുടെ സമാഹാരമാണ് ഈ പുസ്തകം. നവോത്ഥാനം സ്ത്രീജീവിതത്തിലുണ്ടാക്കിയ വിപ്ലവകരമായ പരിഷ്കാരങ്ങളെയും പരിവർത്തനങ്ങളെയുമാണ് അപഗ്രഥനവിധേയമാക്കുന്നു. കേരളത്തിന്റെ സമുദായാധിഷ്ഠിത സാമൂഹ്യഘടനയുടെയും അതിനെ നിർണയിച്ച വർഗ്ഗബന്ധങ്ങളുടെയും പശ്ചാത്തലത്തിൽ നിന്ന് ഓരോ സമുദായവിഭാഗങ്ങൾക്കിടയിലുമുണ്ടായ സാംസ്കാരിക ഉണർവുകളെയും സ്ത്രീശാക്തീകരണ യത്നങ്ങളെയുമാണ് ഇതിൽ വിശദീകരിക്കപ്പെടുന്നത്. ഉച്ചനീചതാങ്ങൾക്കും വിവേചനങ്ങൾക്കും അത്യന്തം ദയനീയമായ അടിമത്വത്തിനുമെതിരെ കേരളീയ സ്ത്രീകൾക്കിടയിൽ ഉണ്ടായ പ്രതിരോധങ്ങളെയും പോരാട്ടങ്ങളെയും ഈ കൃതി അടയാളപ്പെടുത്തുന്നു.

മാറുന്നകാലം മാറുന്ന സ്ത്രീജീവിതം  
ഡോ: എസ്. ശ്രീകുമാരി



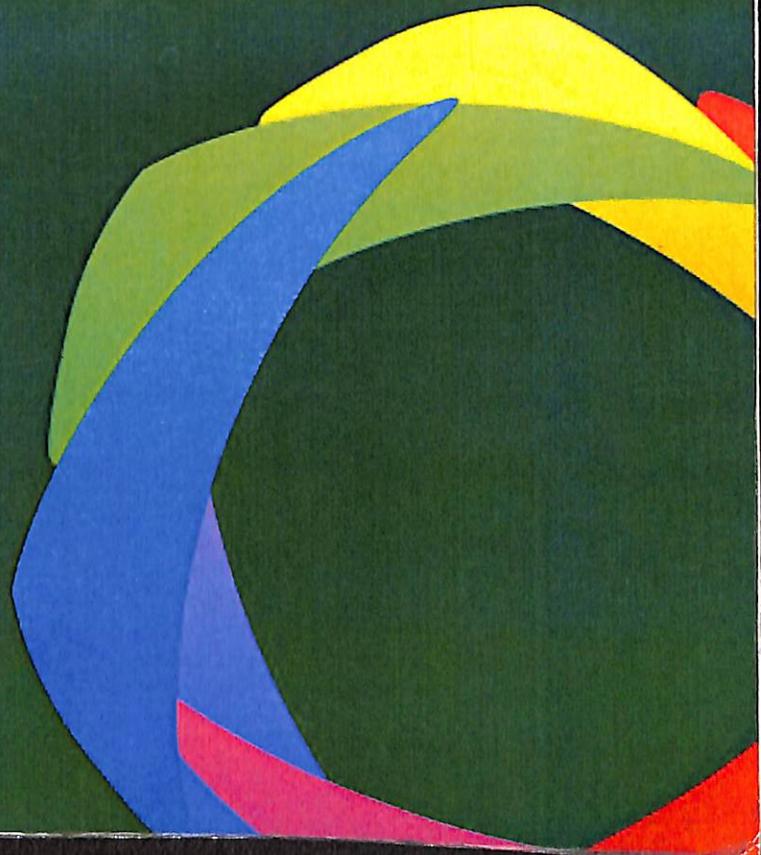
സാംസ്കാരികം  
₹ 130



MAMO  OLLOQUIUM '19

**PROCEEDINGS**  
**OF THE INTERNATIONAL INTERDISCIPLINARY CONFERENCE**  
MAMO COLLEGE , MANASSERY

# Perspective Shift





# Perspective Shift

PROCEEDINGS OF THE INTERNATIONAL INTERDISCIPLINARY CONFERENCE

MAMO  OLLOQUIUM '19

**Chief Editor**

Dr. Abbas T. P

**Editor**

Dr. Ajmal Mueen M. A

**Asst. Editor**

Ms. Hanna Thasneem .S.K

**Editorial Board**

Dr. Aboobacker Mangattuchalil

Dr. Ambil M. K.

Dr. Mumthas P. K.

Ms. Shareena.P.P

Mr. Muhammad Anees P. C

**Design**

Mr. Muhammad Jaffer.V

**April 2019**

© MAMO College, Mukkam

Published by:

**DEPARTMENT OF HISTORY  
V.S.S.D. COLLEGE, KANPUR**

ISBN: 978-81-929384-7-7

# Contents

- 05 **Dr.Shefi.A.E**  
Imparting Knowledge In Pre- Modern Kerala –A Review of Traditional Education System
- 09 **Mujeeb Rahiman.K.G**  
Education in the Social Discourses of Nineteenth Century Malabar
- 12 **Sajith Soman.A**  
Transforming Society of South Malabar & Cultural Trends
- 16 **Febin Sithara**  
A Resolute Voice of Tribals : With Special Reference to Dayabai
- 21 **Twahir.P.H**  
Ahmadiyya Muslim Community & Islamic Revivalism in Kerala –Marginalization & Struggle for Existence
- 25 **Bodhy Krishana.S**  
Comprehensive Study of Wireless Multi-hop Networks
- 29 डॉ अम्बिली एम के.  
लघु विधा के रूप में व्यंग्य का अस्तित्व.
- 31 **Ajith.K**  
Locating Subaltern: Analysis of Vidhu Vincents Film Manhole
- 34 **Hanna Thasneem.S.K**  
Anthropocene Fiction: A Trajectory of Flood Novels
- 37 **Hafsath.U**  
Memories & desires of Diasporic life with special reference to the Malayalam Movie 'Arabikkatha'
- 40 **Nicy Joseph**  
Redefining the Identification Standards of Female : Analysing the Unification of Beauty Identity Cast in the Light of Globalization
- 44 ഡോ.എസ്.ശ്രീകുമാരി  
യാഥാസ്ഥിതികതയുടെ നൂതനമായ തകർത്ത രണ്ടു നാടകങ്ങൾ
- 48 ഡോ.ബിജേഷ്.യു  
ഡൽഹി പ്രവാസി മലയാളികളുടെ സ്വതന്ത്രസംസ്കാരവും അതിജീവനവും
- 52 ബിന്ദു.എം.കെ  
ഇരപ്രവാസം 'അറബുയിലെ അടിമ'യിൽ

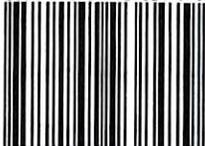
# യാഥാസ്ഥിതികത്വത്തിന്റെ നട്ടെല്ലു തകർത്ത രണ്ടു നാടകങ്ങൾ

ഡോ. എസ്. ശ്രീകുമാരി  
അസിസ്റ്റന്റ് പ്രൊഫസർ  
പ്രോവിഡൻസ് വിമൻസ് കോളേജ്  
കോഴിക്കോട്

ഇരുപതാം നൂറ്റാണ്ടിന്റെ ആദ്യപകുതിയിൽ സജീവമായ സാമൂഹികപരിഷ്കരണ പ്രസ്ഥാനം, ദേശീയ പ്രസ്ഥാനം, ഇടതുപക്ഷപ്രസ്ഥാനം തുടങ്ങിയ സംഘടിത ശ്രമങ്ങളുടെ ഫലമായുണ്ടായ ചിന്താധാരയാണ് നമ്പൂതിരി നവേതാന പ്രസ്ഥാനത്തിന്റെ അന്തഃസത്ത. നമ്പൂതിരി യോഗക്ഷേമസഭയും, യുവജനസംഘടനയും സാമൂഹികസാമൂഹിക പ്രസ്ഥാനങ്ങൾക്ക് നേതൃത്വം നൽകി. 1925 ന് ശേഷം ഉണ്ണി നമ്പൂതിരിയുടെ പ്രസിദ്ധീകരണത്തോടെ നമ്പൂതിരി പരിഷ്കരണ പ്രസ്ഥാനം കൂടുതൽ ശക്തിയാർജ്ജിച്ചു. മുപ്പതുകൾക്ക് ശേഷം സംഘടനയുടെ പ്രവർത്തനത്തിന് നേതൃത്വം നൽകിയത് ഇടതുപക്ഷ രാഷ്ട്രീയപ്രവർത്തകരും, സഹയാത്രികരുമായിരുന്നു. ഈ ഘട്ടത്തിൽ പ്രവർത്തനങ്ങൾക്ക് മാർഗ്ഗനിർദ്ദേശം നൽകിയത് ഓങ്ങല്ലൂർ യോഗമായിരുന്നു. പരമ്പരാഗതമായ സമൂഹഘടനക്ക് മങ്ങലേൽപ്പിച്ചുകൊണ്ട് നൂറ്റാണ്ടുകളായി നിലനിന്നിരുന്ന കുടുംബം, വിവാഹം, ദായക്രമങ്ങൾ എന്നിവ തകരാൻ തുടങ്ങി. നമ്പൂതിരിമാർ മേൽക്കൈ സ്ഥാപിച്ചിരുന്ന അറിവിന്റെ ലോകത്ത്, കോളനി ആധിപത്യത്തിന്റെ സ്വാധീനവും, വിദേശവിദ്യാഭ്യാസത്തിന്റെ പ്രചാരവും മറ്റും വ്യാപകമായപ്പോൾ വിദ്യാഭ്യാസം ജനാധിപത്യവൽക്കരിക്കപ്പെട്ടു. മാറിടയ സാഹചര്യത്തിൽ തങ്ങളുടെ ആധിപത്യത്തിന് അടിസ്ഥാനമായിരുന്ന കുടുംബം ദേവസ്വഭരണങ്ങൾ കാര്യക്ഷമമാക്കുക വ്യവഹാരങ്ങളും ദേശപ്രശ്നങ്ങളും തീർക്കുക, തുടങ്ങി പൊതുപ്രശ്നങ്ങൾ സഭവഴി തീർക്കാൻ തീരുമാനിച്ചു (ഓങ്ങല്ലൂർ യോഗം) നമ്പൂതിരി ആചാരത്തെയോ ആഭിജാത്യത്തെയോ എതിർത്ത് സംസാരിക്കുന്ന രീതിപാടില്ല എന്ന വ്യവ

സ്ഥക്ക് ഈയോഗത്തോടെ മാറ്റം വന്നു. തുടർന്ന്, നമ്പൂതിരി ഇതര സമുദായങ്ങളിൽ ഉണ്ടായ പരിവർത്തനവും അതിന്റെ സ്വാധീനവും നമ്പൂതിരി സമുദായ പരിഷ്കരണത്തിന് ആക്കംകൂട്ടി. നമ്പൂതിരിയോഗക്ഷേമസഭ നമ്പൂതിരി വിദ്യാഭ്യാസത്തിലും ശ്രമം കേന്ദ്രീകരിച്ചു കാലത്തിനൊത്ത വിദ്യാഭ്യാസം നേടുക എന്ന (നമ്പൂതിരി സ്വന്തം പ്രദേശം വിട്ട് പോകാനോ സംസ്കൃതവും മാതൃഭാഷയും അല്ലാതെ മറ്റൊരു ഭാഷ പഠിക്കാനോ അനുവാദം ഉണ്ടായിരുന്നില്ല) ചിന്തപ്രാബല്യത്തിൽ വന്നതിന്റെ ഫലമായിരുന്നു നമ്പൂതിരി പാഠശാലകൾ. നമ്പൂതിരി പാഠശാലകൾ വഴി നമ്പൂതിരിക്ക് വിദ്യാഭ്യാസം, ഉദ്യോഗം തുടങ്ങിയവ സാധ്യമാക്കിയപ്പോഴും നമ്പൂതിരി സ്ത്രീകളെ സമൂഹത്തിന്റെ നേർധാരയിൽ നിന്ന് മാറ്റി നിർത്തുക, ആഭിജാത്യത്തിന് മങ്ങലേൽപ്പിക്കാതെ സൂക്ഷിക്കുക. ജാതിബോധം നിലനിർത്തുക. ആചാരങ്ങളും അനുഷ്ഠാനങ്ങളും തടയുക, പരിഷ്കാരത്തിന്റെ പ്രതീകമായി ഷർട്ട് ധരിക്കാതിരിക്കുക തുടങ്ങിയ ആചാരങ്ങൾ അത്യന്തം നിഷ്ഠയോടെ പാലിച്ചിരുന്നു. നമ്പൂതിരി പാഠശാലയിൽ താമസവും ഭക്ഷണവുമൊക്കെ സൗജന്യമായിരുന്നു. പക്ഷെ പ്രഭാതത്തിലെ കുളി, ക്ഷേത്രദർശനം, ഓത്ത്, നമസ്കാരം തുടങ്ങിയുള്ള മതകാര്യങ്ങളിൽ മുതിർന്ന നമ്പൂതിരിമാരുടെ മേൽനോട്ടം ഉണ്ടായിരുന്നു. സ്കൂൾ സമയം 10 മണിക്ക് ആരംഭിക്കുമ്പോൾ അതിന് മുൻപായി നമ്പൂതിരി ആചാരങ്ങൾ നിർവഹിച്ച ശേഷം ക്ലാസ്സിൽ എത്തുക എന്നതായിരുന്നു നിഷ്കർഷ.

ISBN 978-81-929384-7-9



9 788192 938479 >

April 2019  
© MAMO College, Mukkam

അത്യാം  
**കേരള ചരിത്രം**  
കോൺഫറൻസ്  
പ്രബന്ധങ്ങൾ

THE RUFFLED TIMES IN HISTORY

എഡിറ്റേഴ്സ്

മനോജ് ടി. ആർ., ബിജു ആർ. ഐ.

PROCEEDINGS OF  
Vth INTERNATIONAL  
CONFERENCE ON  
KERALA HISTORY



SPCS

**അഞ്ചാം  
കേരള ചരിത്ര  
കോൺഫറൻസ്  
പ്രബന്ധങ്ങൾ**

PROCEEDINGS OF  
Vth INTERNATIONAL  
CONFERENCE ON  
KERALA HISTORY

കായംകുളം എം.എസ്.എം. കോളേജിൽ നടന്ന  
അഞ്ചാമത് കേരളചരിത്ര കോൺഫറൻസിൽ  
അവതരിപ്പിക്കപ്പെട്ട ശ്രദ്ധേയങ്ങളായ  
പ്രബന്ധങ്ങളുടെ ബൃഹദ് സമാഹാരം.

എഡിറ്റേഴ്സ്  
മനോജ് ടി. ആർ., ബിജു ആർ. ഐ.

 **Sahithya Pravarthaka  
Co-operative Society Ltd.**  
Sales Department  
**National Book Stall**  
Thiruvananthapuram-Kollam-  
Alappuzha-Kottayam- Thiruvalla-  
Thodupuzha- Emakulam -Thrissur-  
Irinjalakuda-Palakkadu-Kozhikodu-  
Kalpatta-Kannur.  
[www.nationalbookstall.com](http://www.nationalbookstall.com)

പ്രബന്ധങ്ങൾ / ₹ 470

ISBN 978-93-88597-11-1



9 789388 597111

**ANCIENT KERALA**

Jain Heritage of Kerala: A Historiographic Critique — Dr. Manoj T. R.	23
--	----

**MEDIEVAL KERALA**

Reconstruction the Myth of Muchilot Bhagavathi — Dr. Susmitha Ramakrishnan	37
Oceanic Trade in Malabar Coast and Tamil Coast: Reconsiderations on Organization of Trade — Dr. M. P. Mujeebu Rehiman	47
Cultural Renaissance of Kerala and Ezhuthachan — SHIKA E.	57
Historicising the Role of Kollam Port in the Maritime History of Kerala — Adabiya H.	68
Socio Cultural Aspects of Sacred Groves in Kerala — Rahumath S.	76
നാടോടിക്കലകളിലെ ജാതിക്രമത്തെ തിരസ്കരിക്കുന്ന പ്രതിബോധം — ഡോ. പ്രിയ ആർ.	83
മൈസൂർ പടയോട്ടം—ചരിത്രമെഴുത്തും രേഖകളുടെ പുതുവായനയും — അനസ് സി. എ.	91

**MODERN KERALA**

Rise of Finance Capitalism and the Expansion of Plantation Industries in Travancore — Anoop. V. S.	101
Re-Imagining the Resistance to Western Medicine in Travancore: With Special Reference to the Subalterns — Ashik Pradeep V.	105
Empowerment of Women and Freedom Struggle of Kerala: Historical Perspective — Bindu. P. S.	110
Space And Urban Landscape: Studying Marine Drive As An Open Space For Human Interaction — Binu K.T.	120

# **Reconstruction the Myth of Muchilot Bhagavathi**

Dr. Susmitha Ramakrishnan

## **Abstract:**

The consciousness of the past and its portrayal are reflected in the myths and practices of the present day. By investigating into the verbal and literary traces of the Theyyam myth, my intention is to create a dialogue between the past and the present and find out how this dialogue in turn constructs the portrayal of the past.

Among the numerous Theyyam Goddesses, here I have analysed a prominent Theyyam Goddess whose legend reveals indigeneous folk origin-the Muchilot Bhagavathi. The gifted Namboodiri girl, became a martyr for fault which was not her own. Since the folk tradition of the Thottam songs was transmitted orally, some transformation might have occurred in the language, but the basic idea of the legend was retained.

Here the myth reveals that even though the Goddess was worshipped, the society never permitted a woman to express herself. A normal woman lived her life and perished unnoticed, it was the aggrieved woman who was worshipped as the Goddess, and that too only after her martyrdom.

Through this paper an attempt is made to analyze the status of women of pre-modern Kerala as evident from the myth of the popular Theyyam.<sup>1</sup>- the Muchilot Bhagavathi. Since the conventional sources of History like inscriptions, manuscripts etc. are generally silent on the status of women, there is a need to analyse other sources which reveal the milieu of pre-modern age. Among the numerous Theyyam forms, the Goddess is very popular as a deity. She is worshipped as the family deity, as the guardian of the village, and also as the protector from dangerous diseases.

By investigating into the verbal and literary traces of the Theyyam tradition, legends, ritual performances, artistic depictions and modes of

DECEMBER 2018

VOLUME 9

ISSN 2319 - 4189

# DIOTIMA'S

## A JOURNAL OF NEW READINGS



**Mythopoesis: Reconstructing Subjugated Knowledges**

**Peer Reviewed Journal**

*Published by*

THE POSTGRADUATE DEPARTMENT OF ENGLISH  
PROVIDENCE WOMEN'S COLLEGE  
KOZHIKODE – 673 009  
KERALA

*(Affiliated to the University of Calicut)*

DECEMBER 2018

VOLUME 9

**DIOTIMA'S**  
**A JOURNAL OF NEW READINGS**



**Mythopoesis: Reconstructing Subjugated Knowledges**

**Peer Reviewed Journal**

*Published by*

THE POSTGRADUATE DEPARTMENT OF ENGLISH  
PROVIDENCE WOMEN'S COLLEGE  
KOZHIKODE – 673 009  
KERALA

*(Affiliated to the University of Calicut)*

web: <https://www.pwcenglish.com/diotimas-a-journal-of-new-readings/>

## **BOARD OF ADVISERS**

**Dr. Jaseena Joseph (Sr. Ashmitha A.C.)**  
Principal, Providence Women's College

**Dr. Janaky Sreedharan**  
Professor, Department of English, University of Calicut

**Dr. S.Nagesh**  
Associate Professor (Retd.), Research Department of English  
St. Joseph's College  
Devagiri, Kozhikode

**Dr. N. Sajan**  
Associate Professor, Research Department of English  
S.N. College, Kannur

**Dr. M.V. Suma**  
Asst. Professor, Department of English  
Govt. College, Kodencheri

## **EDITORIAL BOARD**

Chief Editor  
**Shyama E., HOD Dept. of English**

Editor  
**Dr. Shanthi Vijayan**

### **Members**

**Leeji Francis**  
**Ramani C.E.**  
**Bindu Amat**  
**Dr. Surya K.**

**Dr. Aparna Nandakumar**  
**Elizabeth Antony**  
**Preethy Mary George**  
**Chitra Sebastian**

## CONTENT

December 2018

Volume 9

<b>INTRODUCTION</b> Dr. Shanthi Vijayan	1
<b>RETELLING MYTHS</b> Dr. Janaky Sreedharan	6
<b>THE MYTH OF GENDER ROLES IN FAIRY TALES</b> Rinky Gupta	13
<b>THE GODDESS IN PRE-MODERN KERALA: A FEMINIST ANALYSIS OF THE <i>THEYYAM</i> LEGENDS</b> Dr. Susmitha Ramakrishnan	24
<b><i>WONDER WOMAN: A COMPASSIONATE SEMI-GODDESS IN CONFLICT WITH WORLD WAR I MOTIVES</i></b> Neethu Maria Johnson	39
<b>CRITIQUE OF THE UN/KNOWN: ON THE MEDIATION OF THE 'DOMINANT' ANALYSIS</b> Dr. Sanil M. Neelakandan	49
<b>DISCOVERING THE SELF: ARCHETYPAL ELEMENTS IN <i>CHARLIE</i></b> Alicia Jacob	59
<b>RECONCEPTUALISING INDIAN MYTH IN AMISH TRIPATI'S SHIVA TRILOGY</b> Dr. C. Bhooma	69
<b>THE VOICE OF THE <i>LOKAVRITTA</i> IN MAHASWETA DEVI'S <i>AFTER KURUSHETRA</i></b> Amrutha Modcy	77
<b><i>MS MILITANCY: MYTH AS A COUNTER NARRATIVE</i></b> Harsha Vincent	87
<b>UNLEASHING THE 'SUR-REAL': MYTHOPOETIC IMAGINATION IN SALMAN RUSHDIE'S <i>TWO YEARS EIGHT MONTHS AND TWENTY-EIGHT NIGHTS</i></b> Anila Mohan	100
<b><i>EXTANT</i></b> Shivangi Shanker K.	108
<b><i>THE PERIOD WHEN SHE LEAVES</i></b> Shivshankar Rajmohan A.K.	109

# **THE GODDESS IN PRE-MODERN KERALA: A FEMINIST ANALYSIS OF THE *THEYYAM* LEGENDS**

**DR. SUSMITHA RAMAKRISHNAN**

Through this paper an attempt is made to analyze the status of women in pre-modern Kerala as evident from the popular *Theyyam* cult<sup>1</sup>. Since the conventional sources of History like inscriptions, manuscripts etc. are silent on the status of women, there is a need to analyze other sources like myths and legends that reveal the milieu of a pre-modern age. Among the numerous *Theyyam* forms, the Goddess is very popular as a deity. She is worshipped as the family deity, as the guardian of the village, and also as the protector from dangerous diseases.

By investigating into the verbal and literary traces of the *Theyyam* tradition, legends, ritual performances, artistic depictions and modes of remembrance about the worship of the *Theyyam*, my intention is to create a dialogue between the past and the present and find out how this dialogue in turn constructs a portrayal of the past. The consciousness of the past and its portrayal are as much reflected in the myths and practices of the present day. Many of the ideas taken into consideration here cannot be put under a fixed chronological framework, except that they represent the social category and institutions of pre-modern Kerala. The present enquiry is aimed at an investigation of the pattern of ritual and belief along with their impact on society, in particular on women.

NanoScience and Technology

Patrick Vogt · Guy Le Lay *Editors*

# Silicene

Prediction, Synthesis, Application

 Springer

# **NanoScience and Technology**

## **Series editors**

Phaedon Avouris, IBM Research, Yorktown Heights, USA

Bharat Bhushan, The Ohio State University, Columbus, USA

Dieter Bimberg, Technical University of Berlin, Berlin, Germany

Cun-Zheng Ning, Arizona State University, Tempe, USA

Klaus von Klitzing, Max Planck Institute for Solid State Research, Stuttgart,  
Germany

Roland Wiesendanger, University of Hamburg, Hamburg, Germany

Patrick Vogt · Guy Le Lay  
Editors

# Silicene

Prediction, Synthesis, Application

 Springer

*Editors*

Patrick Vogt  
Institut für Physik  
Technische Universität Chemnitz  
Chemnitz, Germany

Guy Le Lay  
CNRS, PIIM UMR 7345  
Aix-Marseille University  
Marseille, France

ISSN 1434-4904                      ISSN 2197-7127 (electronic)  
NanoScience and Technology  
ISBN 978-3-319-99962-3              ISBN 978-3-319-99964-7 (eBook)  
<https://doi.org/10.1007/978-3-319-99964-7>

Library of Congress Control Number: 2018953713

© Springer Nature Switzerland AG 2018

This work is subject to copyright. All rights are reserved by the Publisher, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in any other physical way, and transmission or information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed.

The use of general descriptive names, registered names, trademarks, service marks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

The publisher, the authors, and the editors are safe to assume that the advice and information in this book are believed to be true and accurate at the date of publication. Neither the publisher nor the authors or the editors give a warranty, express or implied, with respect to the material contained herein or for any errors or omissions that may have been made. The publisher remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

This Springer imprint is published by the registered company Springer Nature Switzerland AG  
The registered company address is: Gewerbestrasse 11, 6330 Cham, Switzerland

# Chapter 1

## A Vision on Organosilicon Chemistry and Silicene



Deepthi Jose, Chandra Chowdhury and Ayan Datta

**Abstract** Replacement of carbon atoms from aromatic molecules and their two-dimensional extended analogues (graphene) have been predicted to have interesting structural diversity and tunable electronic properties. Recent progress in the experimental realization of such systems is discussed along with a conceptual understanding of the structural properties of planar organosilicon compounds and silicene. Pseudo Jahn-Teller (PJT) distortion is shown to contribute to the buckling distortions in silicene which make them excellent materials for band-gap tuning through hydrogenation. Chemical doping of silicene by cations is suggested to be a strategy to suppress buckling of silicene and regain its perfect planar two-dimensional silicon framework. TERS spectroscopy is proposed as a tool to probe the presence or absence of buckling distortions in silicene and cation doped silicene respectively.

### 1.1 Aromatic Molecules and Silicon Substituted Cyclic Rings

The concept of aromaticity or the special stability of cyclic  $\pi$ -conjugated molecules occupies a special position in chemistry. Such molecules are associated with their unusual stability. Manifestation of this stability is seen in their reluctance to undergo several reactions like hydrogenation and oxidation which are much more facile for non-conjugated cyclic molecules. Structurally these molecules are symmetric and vibrationally stable towards distortions to lower symmetry configurations [1]. In 1930s, Hückel proposed a simple model analogous to the tight-binding model popular in solid-state physics for simple cyclic  $\pi$ -conjugated molecules and proposed that

---

D. Jose

Department of Chemistry, Providence Women's College, Calicut 673009, Kerala, India  
e-mail: alphydeepthi@gmail.com

C. Chowdhury · A. Datta (✉)

Department of Spectroscopy, Indian Association for the Cultivation of Science, Jadavpur 700032, West Bengal, India  
e-mail: spad@iacs.res.in

© Springer Nature Switzerland AG 2018

P. Vogt and G. Le Lay (eds.), *Silicene*, NanoScience and Technology,  
[https://doi.org/10.1007/978-3-319-99964-7\\_1](https://doi.org/10.1007/978-3-319-99964-7_1)

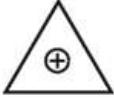
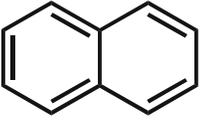
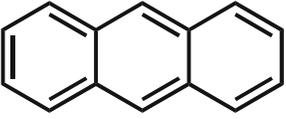
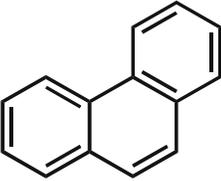
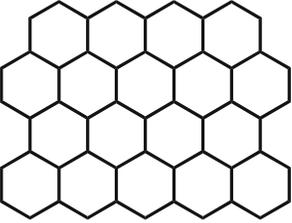
cyclic molecules with  $(4n + 2) \pi$  electrons (where  $n = 0, 1, 2, \dots$ ) should be stabilized due to aromaticity [2–4]. As shown in Table 1.1, several such molecules with integer multiples of  $n$  have been synthesized chemically and characterized by various spectroscopic tools. Of particular mention should be the X-Ray diffraction studies that have shown that these structures are highly symmetric and the bond length alterations (BLA,  $\Delta r$ ) are typically less than 1–2%. The concept of stitching small aromatic molecules in-plane to generate massive two-dimensional graphene like two dimensional materials has been achieved experimentally. Müllen and co-workers have designed atomistically precise graphene nanoribbons based on bottom up synthesis starting from a simple anthracene molecule [5] (linear ( $n = 3$ ) in Table 1.1).

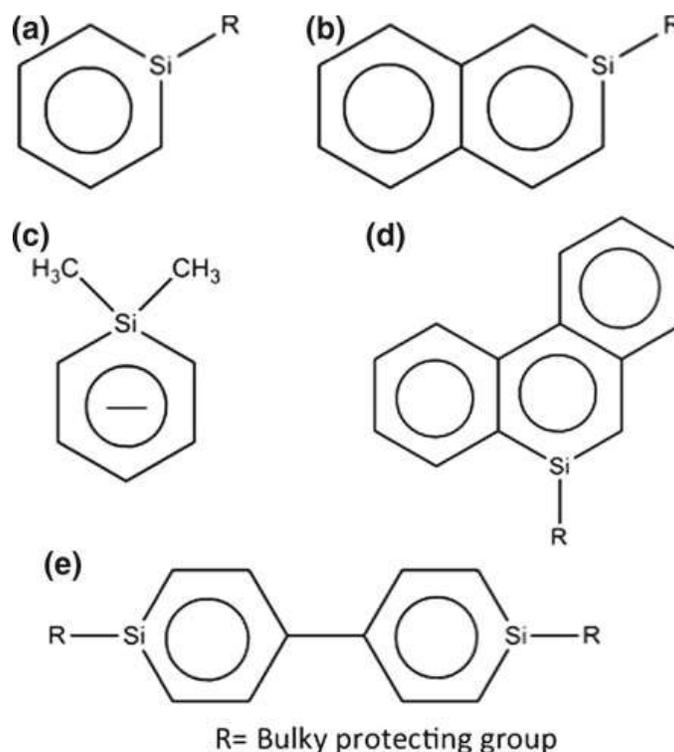
Therefore, for generating two dimensional silicon analogue of benzene namely silicene, one should have a clear understanding of small benzene like silicon rings which might be fused to generate large silicene flakes. In fact, it is with this aim that several groups have pursued the synthesis of silicon substituted aromatic and fused aromatic systems.

In Fig. 1.1, we enlist the experimentally synthesized silicon substituted aromatic molecule. Such sila-aromatic molecules are kinetically labile towards atmospheric oxidation. Therefore, a general experimental strategy to synthesize such molecules has been to use bulky protecting groups which create hydrophobic pockets around these molecules. Tokitoh and co-workers have synthesized silabenzene and silanaphthalene [6, 7] (structures 1(a), 1(b)) and B3LYP/6-31G(d) calculations have revealed that there is a small energy difference between Dewar silabenzene and silabenzvalene, while the planar silabenzene is by far the most stable among the isomers. Jutzi et al. have synthesized the 1,1-dimethyl  $\text{SiC}_5\text{H}_5$  anion (structure 1(c)) which based on structural and qualitative molecular orbital theory calculations has been shown to be aromatic [8]. Sasamori and co-workers have synthesized 9-silaphenanthrene. Crystal structure analysis of 9-silaphenanthrene have shown that the structure remains planar (structure 1(d)) [9]. Based on NMR chemical shifts and NICS calculations, the authors concluded that 9-silaphenanthrene has delocalized  $14\pi$  electron aromatic configuration. Tanabe et al. have synthesized 1,1'-Disila-4,4'-biphenyl (structure 1(e)) [10]. X-ray studies show that both the phenyl rings remain planar and the twist angle of the central C-C bonds between the silaaromatic rings are  $41^\circ$  which is similar to that of biphenyl ( $45^\circ$ ). The UV-vis spectrum of 1,1'-Disila-4,4'-biphenyl showed a red shift and a massive six times enhancement in absorbance compared to that of Tbt-substituted silabenzene. This therefore suggests the existence of extended conjugation through the single bond connecting two silaaromatic rings, a concept well-known in the realms of carbon based on aromatic systems.

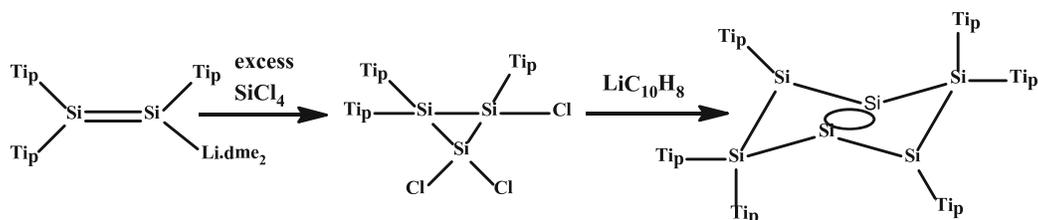
A significant experimental achievement in this area has been the synthesis of an isomer of hexasilabenzene by Abersfelder and co-workers [11]. They synthesized dark green crystals of an isomer of  $\text{Si}_6\text{R}_6$  ( $\text{R} = \text{Tip}, 2, 4, 6\text{-triisopropylphenyl}$  and  $2, 6\text{-diisopropylphenyl}$ ) by the reduction of unsymmetrically substituted trichlorocyclotrisilane (see Fig. 1.2). It has a chair-like conformation in accordance with the theoretical results [12, 13]. Authors propose the term dismutational aromaticity to explain the bonding pattern of this molecule. In order to quantify the aromaticity of the molecule, they calculated the nucleus-independent chemical shift, NICS(0),

**Table 1.1** Existence cyclic stable molecules in line with the predictions from the Hückel model

<b>n</b>	<b>Molecule</b>	<b>Structure and Symmetry</b>
<b>0</b>	<b>Cyclopropyl cation</b>	 $D_{3h}$
<b>1</b>	<b>Benzene</b>	 $D_{6h}$
<b>2</b>	<b>Naphthalene</b>	 $D_{2h}$
<b>3</b>	<b>Anthracene (linear)</b>	 $D_{2h}$
<b>3</b>	<b>Phenanthrene (bent)</b>	 $C_{2v}$
<b>6</b>	<b>Coronene (circular) (Hückel antiaromatic)</b>	 $D_{6h}$
$\infty$	<b>Graphene (flat 2D lattice)</b>	 $C_s$

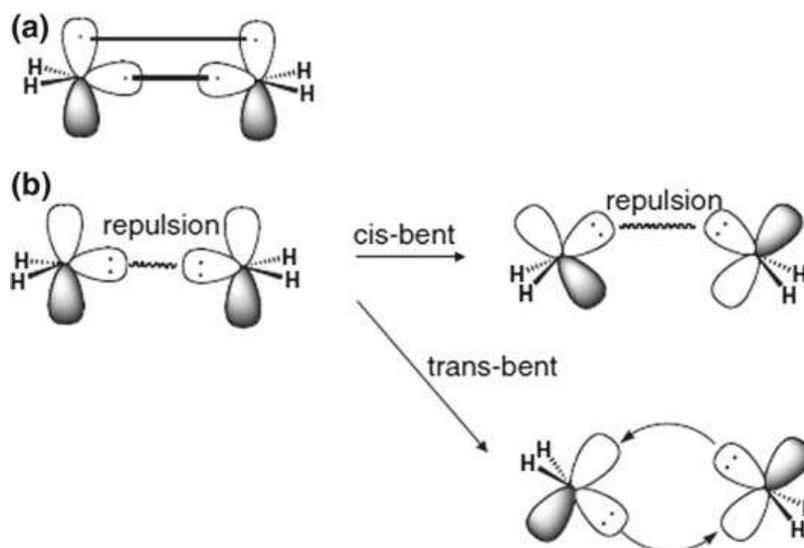


**Fig. 1.1** Experimentally synthesized Sila-aromatic molecules



**Fig. 1.2** Synthesis of the tricyclic isomer of hexasilabenzene (Tip: 2,4,6-triisopropylphenyl; Li.dme<sub>2</sub>: 1,2-dimethoxyethane solvated Li)

at the center of the Si<sub>4</sub> ring (−23.8 ppm), which indicates substantial aromaticity (benzene ~ −10 ppm) but may also include shielding effects from the  $\sigma$ -framework. To estimate these latter effects, they also computed the NICS(0) value for the hypothetical saturated hydrogenation product of the molecule, Si<sub>6</sub>R<sub>6</sub>H<sub>6</sub>. This *in silico* reduction has the effect of sequestering the two Si lone pair electrons and hence suppressing the dismutational resonance. The result (−6.4 ppm) suggests that the strongly diatropic NICS(0) value of Si<sub>6</sub>R<sub>6</sub> is truly due to aromaticity.

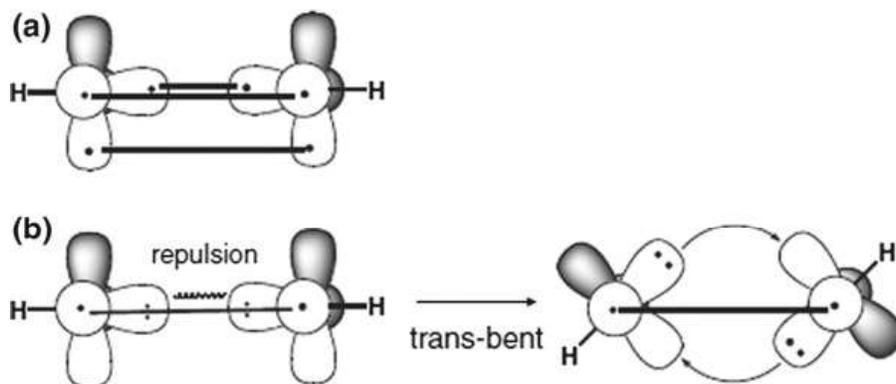


**Fig. 1.3** a Bonding in planar  $\text{H}_2\text{C}=\text{CH}_2$  b Bonding in trans-bent  $\text{H}_2\text{Si}=\text{SiH}_2$ . Reproduced with permission from [14]

## 1.2 Chemical Bonding: Unsaturated Carbon Systems Versus Silicon Systems

The contrasting behavior of the unsaturated carbon systems and their heavier analogues have been discussed in details by Nagase recently [14]. Here we mention the basic features which lead to different structures in silicenes and other two dimensional materials.

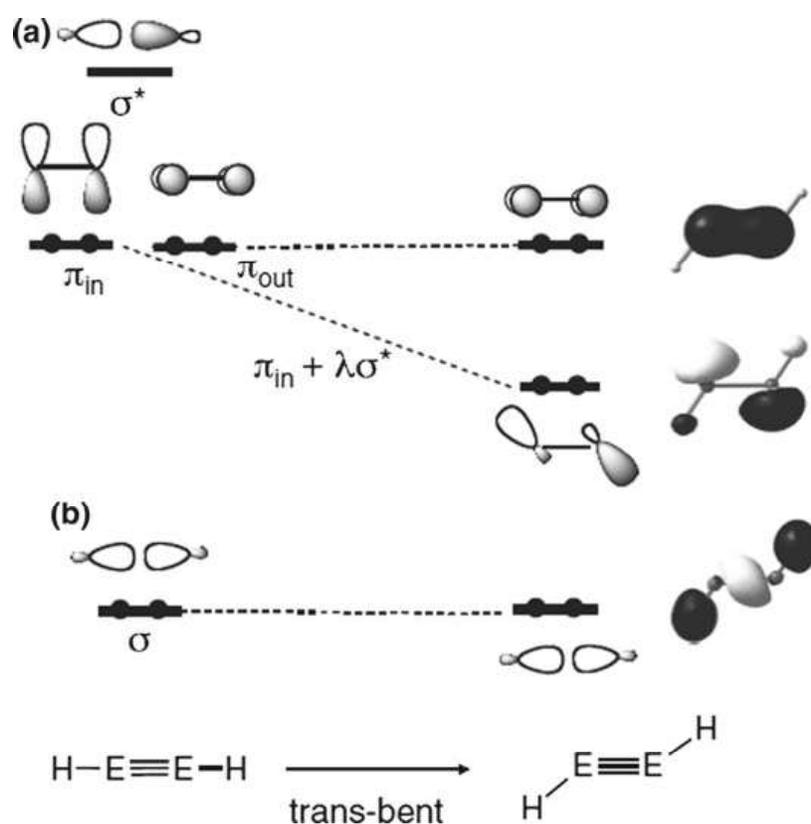
One might envision bonding in  $\text{CH}_2=\text{CH}_2$  or higher unsaturated organic molecules as composed of interaction between two or more  $\text{CH}_2$  fragments. As shown in Fig. 1.3a, each of these  $\text{CH}_2$  units have two unpaired electrons ( $S = 1$ , triplet). These two unpaired electrons are located in a hybridized  $sp^2$  orbital and a perpendicular  $p_z$  orbital respectively. So, as these fragments are brought closer, a maximum overlap between these two orbitals occurs when the overall  $\text{H}_2\text{C}=\text{CH}_2$  unit adapts a perfectly planar configuration (a  $D_{2h}$  point group). However, this case is altered in Silicon hydrides. The ground state of  $\text{SiH}_2$  does not contain unpaired electrons ( $S = 0$ , singlet). So, the two free electrons pair up and are localized as a lone-pair in the  $sp^2$  hybrid orbital (Fig. 1.3b). Hence, now approach of the two  $\text{SiH}_2$  units along the shortest path should lead to strong electron-electron repulsion between the two filled orbitals. The only way to form a  $\text{H}_2\text{Si}=\text{SiH}_2$  bond will be to distort the structure either in a *cis-bent* or a *trans-bent* fashion. Clearly, a *cis-bent* structure should still possess this repulsion albeit in a relatively weaker angular fashion. Therefore, the best orientation of the  $\text{H}_2\text{Si}=\text{SiH}_2$  unit is the distorted *trans-bent* structure. It is important to remember that even though the  $\text{H}_2\text{Si}=\text{SiH}_2$  bond has a formal bond order of two, the *trans-bent* distortion leads to a weaker and hence, relatively longer double bonded system.



**Fig. 1.4** a Bonding in linear HC≡CH b Bonding in trans-bent HSi≡SiH. Reproduced with permission from [14]

Similar to the ethylenic units, the silicon substituted acetylenes, HSi≡SiH also have a *trans-bent* structure. For both CH and SiH, the ground state has one unpaired electron ( $S = 1/2$ , doublet). However, for CH, the excitation energy required to possess three unpaired electrons ( $S = 3/2$ , quartet) is very small ( $\sim 16.7$  kcal/mol). Hence, the CH unit undergoes excitation to reach to a quartet state which facilitates it form three carbon-carbon (one  $\sigma$  and two  $\pi$ ) bonds. This results in a gain in binding energy of 228.5 kcal/mol, a more than ten fold gain compared to the loss in terms of the excitation energy. The formation of a triple bond in HE≡EH is shown schematically in Fig. 1.4a. This results in linear HC≡CH molecule ( $D_{\infty h}$  point group). For SiH, the doublet-quartet excitation energy is much more ( $\sim 36.4$  kcal/mol). Also, the strength of a linear triple bonded HSi≡SiH is expected to be smaller due to poor overlap between the two diffused  $3p_z$  orbitals (formation of one  $\sigma$  bond) and two diffused  $3p_x$  and  $3p_y$  (formation of two  $\pi$  bond, perpendicular to the  $\sigma$  bond and with respect to each other). Therefore, the SiH units prefer to react by orienting their lone-pairs as far as possible as with respect to each other resulting in a *trans-bent* structure as shown in Fig. 1.4b.

One might understand the preference of the HSi≡SiH systems to possess *trans-bent* geometries from the pseudo Jahn-Teller effects (PJTE) [15–17]. As shown in Fig. 1.5, formation of a triple bonded HE≡EH unit ( $E=C, Si$ ) involves filling up of a pair of electrons in one  $\sigma$ -orbital and two pairs of electrons in the in-plane ( $\pi_{in}$ ) and out of plane ( $\pi_{out}$ ) orbitals of  $\pi$ -symmetry. Distortion along the *trans-bent* normal mode,  $Q(\pi_g)$  leads to a symmetry allowed mixing of the filled  $\pi_{in}$  orbital ( $\pi_u$  symmetry) and the empty  $\sigma^*$  orbital ( $\sigma_u$  symmetry). In the case of  $C_2H_2$ , calculations at B3LYP/aug-cc-PVTZ level show that the energy separation between the  $\pi_{in}$  orbital and the  $\sigma^*$  orbital is 8.4 eV making this interaction extremely weak to effectively result in a structural distortion. However, for  $Si_2H_2$ , the  $\pi_{in}-\sigma^*$  gap is only 3.6 eV at the same level of theory. This causes structural instability for the  $D_{\infty h}$  linear structure in  $Si_2H_2$  with an imaginary distortion mode ( $\omega_{\pi_g} = 610.8i$   $cm^{-1}$ ) which on relaxation leads to the *trans-bent* structure of  $Si_2H_2$  of a lower  $C_{2h}$  symmetry. Therefore, a small gap between the filled state (occupied molecular orbital,



**Fig. 1.5** a Bonding in linear  $HC\equiv CH$  b Bonding in trans-bent  $HSi\equiv SiH$ . Reproduced with permission from [14]

OMO) and the empty state (unoccupied molecular orbital, UMO) leads to structural instability in linear  $HSi\equiv SiH$  systems. Such distortions belong to the general class of molecular distortions arising out of small OMO-UMO gaps, a *prime-facie* condition for PJT distortions. In fact, the preference for various heavier analogues of benzene like hexasilabenzene and hexagermanabenzene to have a distorted  $D_{3d}$  geometry instead of the expected planar  $D_{6h}$  geometry has been explained by us based on PJT effect [18]. We discuss this in details in the next section.

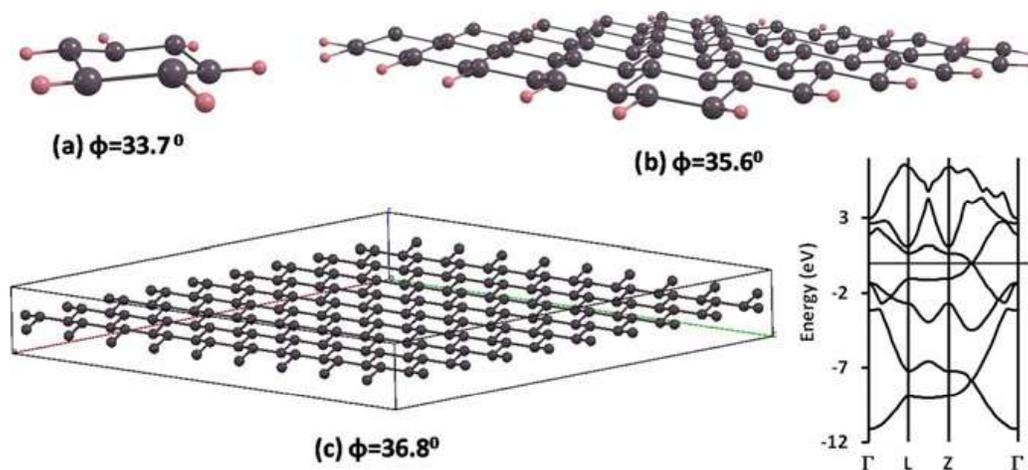
### 1.3 Effect of Buckling Distortions in $Si_6$ Rings: The Psuedo Jahn-Teller (PJT) Effect

Ab initio calculations predict buckled honeycomb geometry for silicene unlike graphene even though it possess similar electronic properties [19, 20]. The symmetry breaking in silicenes by buckling removes the instability associated with the planar high-symmetry structure. Such an instability of high-symmetry geometries of molecular systems is attributed to pseudo-Jahn-Teller (PJT) effect [15, 16]. As suggested by Bersuker, the vibronic coupling between the nondegenerate electronic

states of proper symmetry resulting in nonsymmetric vibrations leads to PJT effect [17, 21, 22]. The sufficiently strong coupling between the unoccupied molecular orbitals (UMOs) with occupied molecular orbitals (OMOs) has been identified and proved to be the source of distortions in many molecular systems [17, 23, 24]. The PJT effect can be suppressed by adding electrons to the UMOs, by increasing the energy gap between the interacting UMO and OMO, or by the isolobal substitution of atom or a group with their more electronegative analogues [25–27]. Puckering in silicene makes it more versatile since, besides having all the exotic properties of graphene, tuning the band gap is much easier [28, 29]. Unlike the ripples in graphene, which are disordered, silicene is puckered in each of the six membered ring and is symmetric across the surface. Because this short-range puckering has a pronounced effect on the electronic properties of silicene it is important to explore the fundamental aspects of puckering distortions and the factors that lead to puckering in silicene. A proper understanding of the buckling distortions is crucial to appreciate the novel properties of silicene and to tune it for various applications.

The silicene clusters gain stability on puckering with increase in the number of rings from  $\text{Si}_6\text{H}_6$  to  $\text{Si}_{70}\text{H}_{22}$  [30]. As shown in Fig. 1.6, the puckering angle  $\phi$  (the dihedral angles between the atoms 1, 2, 3, and 4) for the optimized geometry of  $\text{Si}_6\text{H}_6$  at B3PW91/TZVP is  $33.7^\circ$  and that for  $\text{Si}_{70}\text{H}_{22}$  is  $35.6^\circ$ . Periodic calculations for silicene using VASP plane wave based DFT code find the puckering angle for the optimized silicene sheet is about  $36.8^\circ$  (part c of Fig. 1.6). The puckering distortion in the smallest silicene cluster hexasilabenzene is preserved as such in silicene sheets. The structure, stability and aromaticity of isomers of hexasilabenzene has been studied extensively by various research groups [12, 31, 32]. Among the various isomers hexasilaprismane is computed to be the global minimum in the potential energy surface. The silicon analogue of benzene is 22.7 kJ/mol less stable than hexasilaprismane at CCSD(T)/cc-pVTZ level [33]. Because this  $D_{3d}$  structure is the smallest puckered repeating unit for silicene clusters and sheets, we chose chairlike hexasilabenzene for understanding the puckering distortions.

The strong vibronic coupling of nondegenerate orbitals that are sufficiently close in energy leads to vibrational instability in high symmetry configurations. The symmetry requirement for PJT effect is that the direct product of the symmetries of the nondegenerate orbitals should contain the symmetry of the instability path [34]. The onset of new covalence when a high symmetric configuration moves to a low symmetry configuration is responsible for PJT effect. Its well established in the literature that the planar hexasilabenzene is not a minimum energy isomer and has a vibrational instability (128.8i at M05-2X/6-31 + G(d,p) level of theory) that leads to a  $C_3$  puckered structure [12, 31]. The Si–Si bond length increases from 2.21 to 2.23 Å as hexasilabenzene gets puckered, which is still less than the single Si–Si bond length of 2.35 Å. The planar hexasilabenzene is in  $^1A_{1g}$  electronic structure. The distortion along the unstable  $b_{2g}$  vibrational mode results in the chairlike  $D_{3d}$  structure and the  $b_{2g}$  mode becomes totally symmetric (a) mode. The vibronic coupling between the OMO-UMO pairs: HOMO and LUMO+2, HOMO-1 and LUMO+3 and/or HOMO-4 and LUMO can lead to the distortion of the  $D_{6h}$  structure. The product of the symmetries of OMO-UMO orbitals are:



**Fig. 1.6** Puckering Angle  $\phi$  for **a**  $\text{Si}_6\text{H}_6$ , **b** Large 2D molecular fragment:  $\text{Si}_{70}\text{H}_{22}$ , and **c** Infinite 2D Silicene Sheet with the computed band structure exhibiting the Dirac Cone. Reproduced with permission from [18]

$$\text{HOMO and LUMO} + 2: e_{1g} \times e_{2g} = b_{1g} + b_{2g} + e_{1g}$$

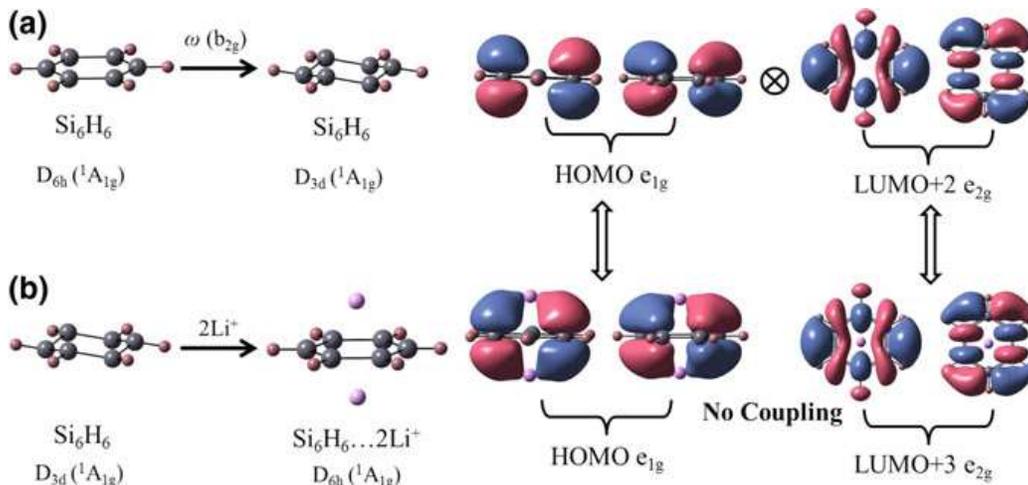
$$\text{HOMO-1 and LUMO} + 3: a_{2u} \times b_{1u} = b_{2g}$$

$$\text{HOMO-4 and LUMO}: e_{1u} \times e_{2u} = b_{1g} + b_{2g} + e_{1g}.$$

The energy gap between these OMO-UMO pairs are 6.83, 8.90, and 9.52 eV, respectively. The vibronic coupling in the OMO-UMO pairs HOMO-1 and LUMO+3 and HOMO-4 and LUMO can be neglected because the energy gap is significantly high. As shown in part a of Fig. 1.7, the PJT distortion due to the coupling between HOMO and LUMO+2 orbitals leads to the puckered  $D_{3d}$  geometry of hexasilabenzene. In the case of planar hexasilabenzene, the overlap of  $\sigma$  and  $\pi$  orbitals is zero. But puckering leads to  $\sigma$ - $\pi$  mixing resulting in a new covalence.

## 1.4 Chemical Functionalization on Silicon Rings to Make Them Planar

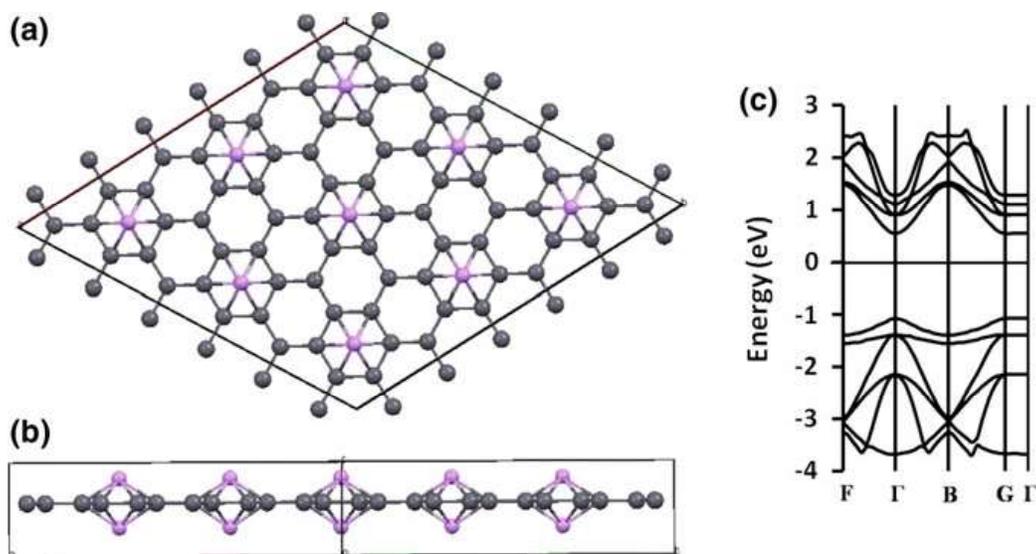
The cation- $\pi$  interactions are widespread and have considerable significance in molecular biology, drug discovery, and supramolecular chemistry [35, 36]. Experimental and theoretical investigations have shown that the cation- $\pi$  binding energies depend on the substituents on the aromatic surface and position and electronegativity of the cation [37, 38]. The origin of cation- $\pi$  interactions in benzene and other aromatic molecules has been mainly attributed to the electrostatic interaction and induction energy [39, 40]. Sergeeva et al. have reported the flattening of pentasilacyclopentadienide ring by suppressing pseudo Jahn-Teller effect using  $\text{Mg}^{2+}$  ions [26]. Ab initio calculations by Zdzetsis predict that  $\text{Si}_6$  can be made planar through



**Fig. 1.7** **a** Onset of puckering from  $D_{6h} \rightarrow D_{3d}$  via  $b_{2g}$  distortion in hexasilabenzene. The corresponding OMO and UMO involved in this vibronic mixing associated PJT are also shown. **b** Suppression of distortion in hexasilabenzene $\cdots 2\text{Li}^+$ . The 1–1 correspondence between the OMO and UMO are shown with respect to the undoped hexasilabenzene. (Calculations were done at M05-2X/6-31+g(d,p) level.) Reproduced with permission from [18]

the reduction of  $\text{Si}_6^{6-}$  anion in the presence of counter cations. The resulting  $\text{Si}_6\text{Li}_6$  is planar, stable, and aromatic [41]. We performed DFT calculations to investigate whether the  $\pi$ -surface of hexasilabenzene can bind a metal ion. In the presence of  $\text{Li}^+$ , the puckered  $\text{Si}_6$  ring of hexasilabenzene becomes planar to form a stable  $C_{6v}$   $\text{Si}_6\text{H}_6 \cdots \text{Li}^+$  complex. The BSSE corrected binding energy for hexasilabenzene with  $\text{Li}^+$  is  $-45.3$  kcal/mol. The corresponding value for benzene $\cdots \text{Li}^+$  complex is  $-39.9$  kcal/mol. The distance between the metal ion and the centroid of the ring is  $1.94$  Å.  $\text{Li}^+$  ion not only binds with hexasilabenzene more strongly than benzene but also suppresses the PJT distortion in hexasilabenzene ring. The energy gap of the OMO-UMO pair of hexasilabenzene increased from  $6.83$  to  $7.37$  eV in the presence of a  $\text{Li}^+$  ion. The increase in energy gap in presence of  $\text{Li}^+$  is sufficient enough to quench the coupling of OMO-UMO pair thereby suppressing the PJT effect along the  $b_{2g}$  mode. The  $\pi$ -surface of aromatic rings can be tuned to accommodate two cations [42]. We calculated the binding energy of hexasilabenzene with two  $\text{Li}^+$  ions. Unlike benzene for which binding of two cations on either side of the aromatic ring is endothermic, hexasilabenzene forms a stable  $D_{6h}$   $\text{Si}_6\text{H}_6 \cdots 2\text{Li}^+$  complex and the BSSE corrected binding energy is  $-3.5$  kcal/mol. The distance between the metal ion and the centroid of the ring is  $2.18$  Å. The electrostatic field from the two  $\text{Li}^+$  ions increases the OMO-UMO energy gap to  $7.68$  eV restoring high symmetry  $D_{6h}$  structure of hexasilabenzene. Part b of Fig. 1.7 shows the suppression of PJT distortion of hexasilabenzene in the presence of two  $\text{Li}^+$  ions. The one-to-one correspondence between the OMO and UMO of hexasilabenzene and the 2:1  $\text{Li}^+$  doped hexasilabenzene are also shown.

Inspired by the results for planarization for hexasilabenzene on mono and di lithiation, material with planar silicene sheet decorated with  $\text{Li}^+$  were designed and



**Fig. 1.8** **a** Transverse view, **b** lateral view of optimized  $\text{Li}^+$ -decorated silicene sheet, **c** its band structure (at the GGA/PBE level with plane wave basis). Reproduced with permission from [18]

periodic calculations were performed for such extended system. The unit cell was constructed such that the  $\text{Li}^+$  ions bind to the top and bottom surface of alternate hexasilabenzene ring. In agreement with the results of hexasilabenzene, the silicene sheet turns planar in the presence of  $\text{Li}^+$  ions. The transverse and lateral view of a  $3 \times 3$  supercell of the optimized  $\text{Li}^+$  decorated silicene cluster is shown in Fig. 1.8. The presence of  $\text{Li}^+$  ions open up the band gap in silicene (part c of Fig. 1.5). The band gaps for silicene $\cdots\text{Li}^+$  and silicene $\cdots 2\text{Li}^+$  are calculated to be 1.29 and 1.25 eV, respectively. The band gaps are estimated to be 1.70 and 2.14 eV (1.62 and 2.10 eV) at HSE06 and B3LYP hybrid levels of calculations for silicene $\cdots\text{Li}^+$  (silicene $\cdots 2\text{Li}^+$ ), respectively.

## 1.5 Electron and Hole Transport in Silicene

The Reorganization Energy ( $\lambda$ ) can give an insight into the charge transfer properties of the system. The reorganization energy is a key factor controlling the rate of charge transport in a system within an incoherent charge transport method. The energy required for the structural changes of the molecule when an electron is added or removed is the internal reorganization energy, and the external reorganization energy is due to structural modifications in the surrounding medium during the electron transfer process. The molecules with small reorganization energies are in high demand due to their numerous applications in the electronic and optoelectronic industries. The internal reorganization energy for the silicenes has been calculated at B3PW91/TZVP level using the relation [43]:

$$\lambda_{\text{hole/electron}} = (E_{\pm}^* - E_{\pm}) + (E_{\text{cation/anion}}^* - E)$$

where  $E$  is the energy of neutral state in the neutral geometry,  $E_{\text{cation/anion}}^*$  is the energy of the neutral state in the cationic/anionic geometry,  $E_{\pm}$  is the energy of cationic/anionic state in that geometry and  $E_{\pm}^*$  is the energy of cationic/anionic state in the neutral geometry. The reorganization energy for the silicenes in the are reported in Table 1.2. For all the silicenes the  $\lambda_{\text{hole}}$  value is smaller than  $\lambda_{\text{electron}}$ . This is an important result, since polyacenes are also known to be hole conductors. The  $\lambda_{\text{hole}}$  values for PAH,  $\text{C}_{10}\text{H}_8$ ,  $\text{C}_{14}\text{H}_{10}$ ,  $\text{C}_{18}\text{H}_{12}$  and  $\text{C}_{22}\text{H}_{14}$  at B3LYP/6-31G\*\* are 0.18, 0.14, 0.11 and 0.97 eV, respectively [44]. This is in good agreement with the values that we calculated for the corresponding silicon analogues  $\text{Si}_{10}\text{H}_8$  (0.16 eV),  $\text{Si}_{14}\text{H}_{10}$  (0.13 eV),  $\text{Si}_{18}\text{H}_{12}$  (0.12 eV) and  $\text{Si}_{22}\text{H}_{14}$  (0.10 eV). Therefore, silicenes might be considered as “*sister molecules*” to polyacenes. The reorganization energy decreases as the value of  $m$  and  $n$  increases, which can be utilized for a wide variety of applications in electronics. The  $\lambda_{\text{hole}}$  and  $\lambda_{\text{electron}}$  values for various silicenes suggest that with the increase in the values of  $m$  and  $n$ , silicenes show amphiphilic character. The puckering in the dihedral of peripheral hexasilicene rings increases with the addition of an electron and decreases with the removal of an electron compared to the neutral species. This difference is negligible as the number of rings increase, which implies that the charges get delocalized for larger clusters.

It is important to note that bulk Si is known to exist in only  $sp^3$  covalently link diamond-like structure, [45] which might be visualized as layers of puckered silicenes stacked over one another with the  $\text{C}_3$  distortions arising from the additional interlayer Si–Si bonds. This is in contrast to carbon that exists additionally in the pure  $sp^2$  graphite structure. Thus, the absence of any other allotrope of Si similar to the graphite form in carbon can be attributed to the puckering distortion that renders  $\pi$ -stacking interactions ineffective through the loss of planarity in each six-membered ring, and favors an  $sp^3$  bonding environment. Also, the diamond structure of Si ensures that Si–Si interaction energies are identical both along the layer and in between the layers. To understand the interaction between the layers, the bonding energies of the interlayer structures were computed at the same level of theory. Basis set superposition error (BSSE) was corrected using the counterpoise correction (CP) method [46].

For the dimers the Si–Si bond length varies between 2.37 and 2.39 Å along the interlayer for different sized systems, which is comparable with the bulk Si–Si bond length of 2.35 Å. The Si–Si bond length in between the layers are in the range 2.38–2.47 Å. A HOMO-LUMO gap of 2–3 eV suggests semiconducting behavior for the dimers. A higher value of the HOMO–LUMO gap compared to the corresponding monomers indicates that delocalization is more in the plane. The transfer integral in between the monomers for the dimer was calculated using the relation [47, 48].

$$t_{\text{hole}} = 1/2\{E(\text{HOMO}) - E(\text{HOMO} - 1)\}$$

$$t_{\text{electron}} = 1/2\{E(\text{LUMO} + 1) - E(\text{LUMO})\}$$

**Table 1.2** Binding energy per Si atom (eV), point group, HOMO-LUMO (eV), reorganization energy for silicenes of various nuclearities at B3PW91/6-31G(d) level of theory

Molecule	Average puckering angle	Binding energy/atom	HOMO-LUMO Gap	$\lambda_{\text{hole}}$	$\lambda_{\text{electron}}$
Si <sub>6</sub> H <sub>6</sub>	33.7	-0.90	3.22	0.26	0.96
Si <sub>10</sub> H <sub>8</sub>	34.3	-0.93	2.26	0.16	0.47
Si <sub>14</sub> H <sub>10</sub>	34.4	-0.94	1.68	0.13	0.25
Si <sub>14</sub> H <sub>10</sub>	34.8	-0.95	2.21	0.16	0.48
Si <sub>18</sub> H <sub>12</sub>	34.3	-0.95	1.31	0.12	0.15
Si <sub>22</sub> H <sub>14</sub>	34.3	-0.95	1.06	0.10	0.14
Si <sub>16</sub> H <sub>10</sub>	35.0	-0.97	1.80	0.13	0.31
Si <sub>22</sub> H <sub>12</sub>	35.2	-0.98	1.35	0.11	0.22
Si <sub>28</sub> H <sub>14</sub>	35.2	-0.99	1.03	0.12	0.17
Si <sub>24</sub> H <sub>12</sub>	36.7	-1.00	1.89	0.11	0.20
Si <sub>30</sub> H <sub>14</sub>	35.4	-1.00	1.02	0.09	0.18
Si <sub>34</sub> H <sub>16</sub>	35.2	-0.99	0.80	0.08	0.16
Si <sub>38</sub> H <sub>16</sub>	35.4	-1.00	0.78	0.08	0.15
Si <sub>46</sub> H <sub>18</sub>	35.5	-1.01	0.60	0.08	0.17
Si <sub>48</sub> H <sub>18</sub>	35.5	-1.01	0.59	0.07	0.13
Si <sub>58</sub> H <sub>20</sub>	35.6	-1.02	0.44	0.06	0.11
Si <sub>70</sub> H <sub>22</sub>	35.6	-1.03	0.33	0.06	0.10

The binding energies, reorganization energies, HOMO-LUMO gaps and the transfer integral for the dimers are given in Table 1.3. The binding energies calculated at B3PW91 and M05-2X levels are consistent with each other, which implies that dispersion interactions do not make a significant contribution in stabilizing the silicene dimers, unlike in the carbon analogues. The structures for the stacked dimers of the monomeric layers are shown in Fig. 1.9. One clearly observes that unlike  $\pi$ -stacking interactions in PAH, covalent Si-Si bonding stabilizes the interlayer bonding. It is interesting to note that both the  $t_{\text{hole}}$  and  $t_{\text{electron}}$  are about 20% of that for organic molecules like TTF, TCNQ, BTQBT, benzene and naphthalene [47, 49]. The lower values of the transfer integrals arise due to smaller spacing between the valence and conduction levels as a consequence of the more diffused orbitals on silicon compared to carbon.

## 1.6 Reactivity of Silicene Towards Hydrogen and Band Gap Tuning

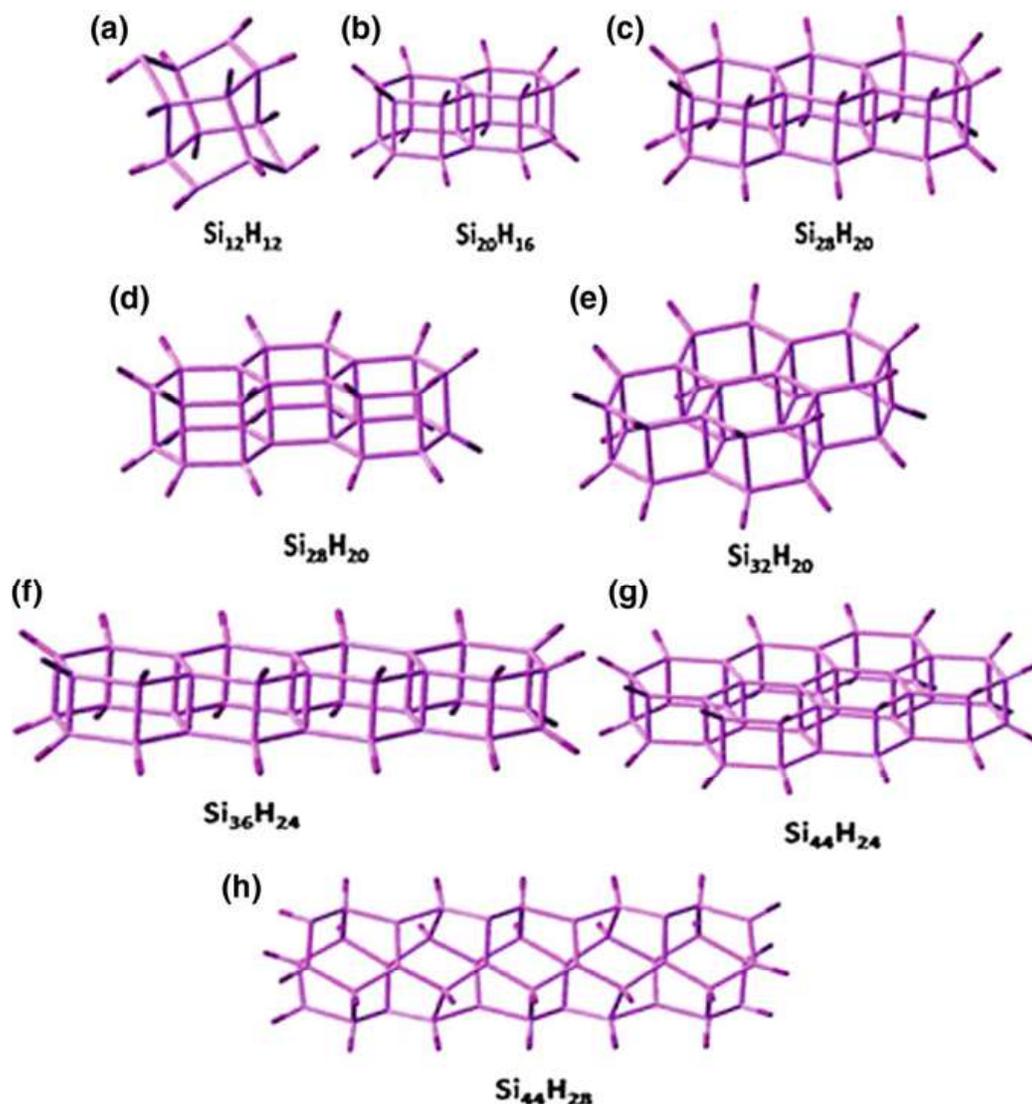
It has been already reported that the hydrogenation of a single-layer of graphene causes remarkable changes in the electronic and atomic structures, and in the trans-

**Table 1.3** Binding energy of the co-facial dimers (in eV), hole and electron reorganization energies (in eV) HOMO–LUMO (eV) and hole and electron transfer integrals (in eV) for silicenes of various nuclearities at B3PW91/6-31G(d) level of theory

Dimer	Binding energy per monomer	$\lambda_{\text{hole}}$	$\lambda_{\text{electron}}$	HOMO-LUMO gap	Transfer integral ( $t_{\text{hole}}$ )	Transfer integral ( $t_{\text{electron}}$ )
Si <sub>12</sub> H <sub>12</sub>	−3.6	0.27	1.51	2.0	0.05	0.08
Si <sub>20</sub> H <sub>16</sub>	−9.2	0.90	0.35	3.1	0.15	0.17
Si <sub>28</sub> H <sub>20</sub>	−12.3	0.76	0.34	2.8	0.11	0.03
Si <sub>28</sub> H <sub>20</sub>	−12.0	0.56	0.28	2.5	0.19	0.21
Si <sub>32</sub> H <sub>20</sub>	−13.0	0.52	0.15	2.3	0.15	0.019
Si <sub>36</sub> H <sub>24</sub>	−15.7	0.64	0.27	2.6	0.03	0.05
Si <sub>44</sub> H <sub>24</sub>	−16.6	0.56	0.16	2.0	0.04	0.06
Si <sub>44</sub> H <sub>28</sub>	−17.1	1.16	1.36	1.8	0.03	0.07

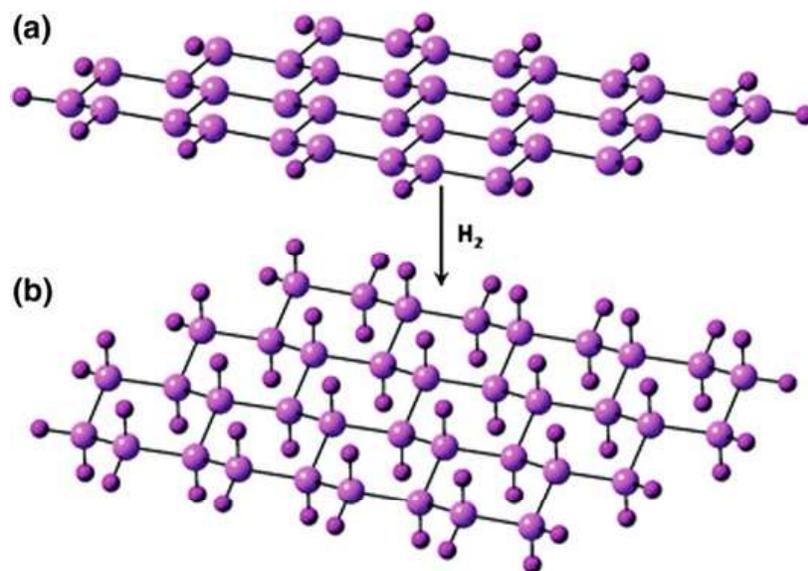
port properties. The successful synthesis of hydrogenated graphene (graphane) was first accomplished by Elias et al. [50]. Though the hydrogenation process is reversible, the graphane formed with  $sp^3$  hybridized carbon atoms in the lattice is stable at room temperature for many days. It is crystalline and retains the hexagonal lattice, but the periodicity is considerably shorter compared to graphene. The hydrogenation increases the energy gap in graphane and conductance becomes temperature dependent. Annealing the graphane at high temperature restores many of the fundamental properties of graphene, like metallic state, the lattice spacing and the quantum Hall effect. An earlier theoretical calculation by Sofo et al. predicted that the chair-like conformer, with hydrogen atoms bonded to carbon on both sides of the plane in an alternating manner, is more stable than a boat-like conformer in which a pair of hydrogen atoms occupy alternate positions. Graphane also has a very high volumetric and gravimetric hydrogen density, and hence has promising applications [51]. It is interesting to study the feasibility of the hydrogenation reaction of silicenes and its effect on the different properties and structure of silicene. The stability of hydrogenated silicon fullerenes has been studied by various research groups, and they are proven to have a potential hydrogen storage capacity. An efficient and low cost storage material for hydrogen is a major challenge for the current scientific community, and this is an area of active research. The US Department of Energy hydrogen storage system targeted a 6.0 weight percent gravimetric capacity and a volumetric capacity of 0.045 kg L<sup>−1</sup> for the year 2010 [52]. Previous first principle calculations by Cao et al. revealed that silicon nanotubes are better candidates for hydrogen storage compared to iso-diameter carbon nanotubes. The denser and more localized electron clouds of silicon nanotubes can adsorb hydrogen more strongly [53].

The structures of silicenes with different nuclearity were optimized after saturating all the bonds with hydrogen atoms. The heat of hydrogenation is calculated using the relation  $\Delta H = H(\text{Si}_a\text{H}_{b+c}) - (H(\text{Si}_a\text{H}_b) + c/2 \text{H}_2)$ , where  $c$  is the number of hydrogen molecules added for complete saturation (see Fig. 1.10). The result shows that the



**Fig. 1.9** The optimized “tiffin-box like” structures for the stacked dimers of the silicene strips at B3PW91/6-31 G(d) level of theory. Reproduced from [30] with permission from PCCP Owner Societies

reaction is more exothermic than the carbon counterparts. The heat of hydrogenation for benzene, naphthalene, anthracene and phenanthrene is  $-2.16$  eV,  $3.5$  eV,  $5.0$  eV and  $4.7$  eV, respectively, [54] which in the silicon world for  $\text{Si}_6\text{H}_6$ ,  $\text{Si}_{10}\text{H}_8$ , the anthracene analogue of Si,  $\text{Si}_{14}\text{H}_{10}$  and the phenanthrene analogue of Si,  $\text{Si}_{14}\text{H}_{10}$ , are  $-4.63$ ,  $-7.48$ ,  $-10.40$  and  $-10.25$  eV. The instability of  $sp^2$  silicon in silicene compared to  $sp^2$  carbon in graphene makes hydrogenation more feasible in the case of silicene. The weight percent of hydrogen for various silicenes (values for carbon analogues in the parenthesis) are given in Table 1.4, and it ranges from 6.6 to 4.5%. The preference of Si to be in an  $sp^3$  environment rather than an  $sp^2$  environment is evident from the structural parameters. The Si-Si bond length in hydrogenated



**Fig. 1.10** Schematic representation of structural changes in silicene clusters on hydrogenation. Reproduced from [30] with permission from PCCP Owner Societies

silicenes is between 2.35 and 2.36 Å, which agrees well with the standard value of 2.35 Å. The Si–Si–Si bond angles are in the range 110–111°, and Si–Si–H bond angles range between 107 and 109°. The HOMO–LUMO gap and polarizability of the hydrogenated silicenes are also given in Table 1.4. All the silicenes under our study have HOMO–LUMO gaps greater than 4 eV, indicating a shift from the zero gap semiconductor realm to that of wide gap semiconductors. The increase of the band gap during saturation of silicenes with hydrogens can be used for band gap tuning by controlled saturation by hydrogen. Though the storage capacities of these clusters are comparatively lower than PAH, coupled with their band engineering properties silicenes can be seen as promising materials.

## 1.7 Tip Enhanced Raman Spectroscopy (TERS) as a Probe for the Buckling Distortion in Silicene

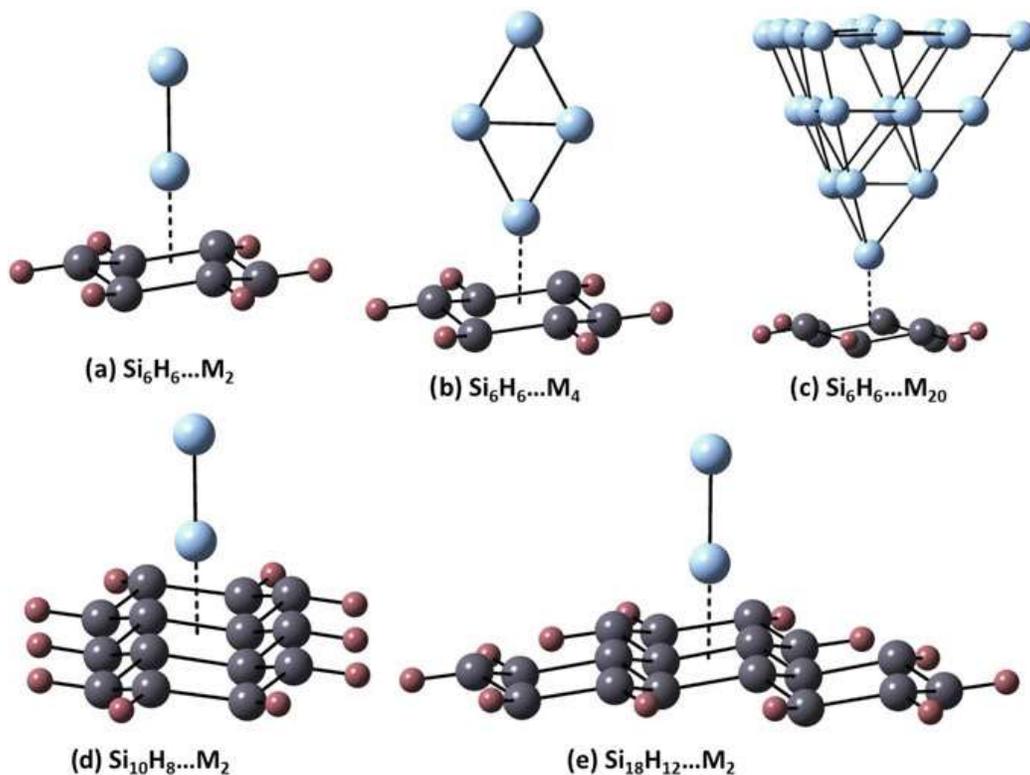
Raman spectroscopy is a significant tool for the characterization of 2D materials. The Raman spectrum of graphene has been shown to evolve with the number of layers and can be effectively used to differentiate monolayer, bilayer and multilayer graphene [55]. This non-destructive technique is also sensitive towards the quality of layers, doping level and defects in the graphene sheet [56]. Scalise et al. have calculated the Raman spectrum of free standing silicene and germanene and also the nanoribbons of Si and Ge [57]. They found that silicene shows an intense G-like peak at 570  $\text{cm}^{-1}$ . Corresponding to the D peak in graphene, Si nanoribbons show a peak at 515  $\text{cm}^{-1}$ . Cinquanta et al. have reported the Raman spectrum of epitaxial silicene [58]. They found that the interaction of Si atoms with the Ag(111)

**Table 1.4** Heat of hydrogenation, HOMO–LUMO gap, polarizability and weight percent of H for hydrogenated silicenes (silicanes) of various nuclearities

Species	Heat of hydrogenation (eV)	Heat of hydrogenation/Si-atom	HOMO-LUMO gap (eV)	Polarizability (a.u.)	% wt. of hydrogen
Si <sub>6</sub> H <sub>12</sub>	−4.63	−0.77	6.97	175.63	6.6
Si <sub>10</sub> H <sub>18</sub>	−7.48	−0.75	5.96	307.51	6.0
Si <sub>14</sub> H <sub>24</sub>	−10.40	−0.74	5.35	425.41	5.7
Si <sub>14</sub> H <sub>24</sub>	−10.25	−0.73	5.54	445.59	5.7
Si <sub>18</sub> H <sub>30</sub>	−13.34	−0.74	5.00	606.28	5.6
Si <sub>22</sub> H <sub>36</sub>	−16.29	−0.74	4.78	766.09	5.5
Si <sub>16</sub> H <sub>16</sub>	−11.35	−0.71	5.48	507.29	3.4
Si <sub>22</sub> H <sub>34</sub>	−15.61	−0.71	5.01	734.18	5.2
Si <sub>28</sub> H <sub>42</sub>	−19.77	−0.71	4.70	969.62	5.0
Si <sub>24</sub> H <sub>36</sub>	−17.70	−0.74	5.12	798.21	5.0
Si <sub>30</sub> H <sub>44</sub>	−20.94	−0.70	4.81	1037.82	5.0
Si <sub>34</sub> H <sub>50</sub>	−23.95	−0.70	4.49	1214.41	5.0
Si <sub>38</sub> H <sub>54</sub>	−26.32	−0.69	4.54	1357.97	4.8
Si <sub>46</sub> H <sub>64</sub>	−31.68	−0.69	4.37	1690.37	4.7
Si <sub>48</sub> H <sub>66</sub>	−32.87	−0.68	4.45	1766.55	4.7
Si <sub>58</sub> H <sub>78</sub>	−39.46	−0.68	4.28	2189.89	4.6
Si <sub>70</sub> H <sub>92</sub>	−47.23	−0.67	4.22	2040.75	4.5

surface distorts the low buckled silicene structure and enlarges the unit cell. The intense sharp peak at  $516\text{ cm}^{-1}$  resembling the G-peak of graphene is a fingerprint of silicene. Calculations have been performed on free standing silicene clusters to capture the signature of buckling distortion in the Raman spectrum and enhance the intensity of this particular normal mode using metal clusters [59]. The vertical displacement of alternate Si atoms of each hexagonal ring along the  $C_{3v}$  axis leads to the buckling distortion in silicene. Since the dipole moment of the molecule is not changing during the buckling distortion, infrared (IR) spectroscopy cannot track this effect.

The vibrational frequencies and Raman intensities for various clusters of silicene were calculated. In order to examine the effect of metal clusters on Raman intensity, the silicene clusters: Si<sub>6</sub>H<sub>6</sub>, Si<sub>14</sub>H<sub>10</sub> and the fused cluster Si<sub>18</sub>H<sub>12</sub> were chosen. The clusters of gold and silver are considered to be adsorbed on the silicene surface. The M<sub>2</sub>, M<sub>4</sub> and M<sub>20</sub> clusters of Au and Ag were placed at a distance of 2.5 Å from the center of mass of silicene clusters from the tip of the cluster as shown in Fig. 1.11. The distance of 2.5 Å is selected based on the most stable vertical configuration of the metal dimer (M<sub>2</sub>). The ECP basis set LANL08(f) [60–62] available from the EMSL Basis Set Exchange Library [63, 64] was employed for the metal atoms.



**Fig. 1.11** Silicene fragments with metal clusters adsorbed over the surface ( $M = \text{Au, Ag}$ ). Reproduced from [59] with permission from PCCP Owner Societies

The high sensitivity of surface-enhanced Raman scattering (SERS) has made it a powerful analytical technique [65–67]. The combination of scanning probe microscopy (SPM) and SERS, Tip-enhanced Raman scattering (TERS), is promising with added advantages like uniform enhancement of the signal at all sample locations, high spatial resolution, coupling of topographic features with spectroscopic data, quantitative measurement of SERS etc. [68, 69]. In TERS, the SPM tip is an externally tunable hot spot and one can effectively use it to enhance the Raman signal. Clusters of silver and gold to model the tip and study its effect on the Raman spectra of the silicene cluster. The buckling frequency, Raman scattering activity, enhancement in the scattering activity and binding energy for the silicene clusters  $\text{Si}_6\text{H}_6$ ,  $\text{Si}_{14}\text{H}_{24}$  and  $\text{Si}_{18}\text{H}_{12}$  in the presence of metal clusters are given in Table 1.5. The enhancement in the scattering activity is calculated as the ratio of scattering activity for the buckling mode of the silicene-metal complex to the scattering activity of the most prominent buckling mode of the corresponding silicene cluster. While, the enhancements are modest (in between 2–5 times increase), the enhancements increase with an increase in the size of the metal cluster. For example, for hexasilabenzene ( $\text{Si}_6\text{H}_6$ ) the enhancement increases from 1.1 to 4 times as a gold cluster increases in size from a simple linear dimer to a tetrahedral  $\text{Au}_{20}$ . Much stronger manifestation occurs when the tip is considered to be silver. The enhancement increases from 3 times to 17 times as the size of the Ag cluster increases from 2 to 20.

**Table 1.5** The buckling frequency, scattering activity, enhancement in scattering activity and binding energy for silicene fragments in the presence of metal clusters at the M05-2X/TZVP level of theory

Species	Buckling frequency (cm <sup>-1</sup> )	Scattering activity (S.A) (Å <sup>4</sup> /AMU)	Enhancement in S.A	Binding energy (kcal mol <sup>-1</sup> )
Si <sub>6</sub> H <sub>6</sub> ...Au <sub>2</sub>	104	25.87	1.1	-26.0
Si <sub>6</sub> H <sub>6</sub> ...Au <sub>4</sub>	97	52.11	2.22	-22.3
Si <sub>6</sub> H <sub>6</sub> ...Au <sub>20</sub>	100	95.24	4.05	-25.4
Si <sub>6</sub> H <sub>6</sub> ...Ag <sub>2</sub>	100	75.28	3.21	-18.0
Si <sub>6</sub> H <sub>6</sub> ...Ag <sub>4</sub>	80	169.84	7.23	-14.1
Si <sub>6</sub> H <sub>6</sub> ...Ag <sub>20</sub>	109	402.08	17.1	-18.6
Si <sub>14</sub> H <sub>10</sub> ...Au <sub>2</sub>	139	76.75	1.36	-25.3
Si <sub>14</sub> H <sub>10</sub> ...Ag <sub>2</sub>	142	103.5	1.84	-17.7
Si <sub>18</sub> H <sub>12</sub> ...Au <sub>2</sub>	97	18.38	1.47	-22.5
Si <sub>18</sub> H <sub>12</sub> ...Ag <sub>2</sub>	131	91.43	1.81	-15.3

## Outlook and Future Perspectives

The bottom up design of two dimensional silicon based materials from basic starting point namely silicon substituted benzene and stitching atoms with perfection along a honeycomb is challenging. Over the last decade, synthetic chemist aided by concepts of theoretical chemistry have been able to design higher order molecular fragments of fused aromatic molecules where the carbon atoms have been replaced by silicon. One should expect bigger molecular fragments with 10–15 fused six membered rings of silicon being synthesized.

Calculations and experiments have now established that unlike graphene, silicene will be buckled which is understood on the basis of Pseudo Jahn-Teller distortions in silicon systems. Computational studies predict that intercalation of cations between the silicene layers led to suppression of the buckling distortion and the graphene like structural feature can be regained. Aromatic organosilicon compounds have excellent transport properties and the band gap can be tuned by chemical functionalization. One might anticipate that rapid progress in synthesis of such molecules would provide new insights into various aspects of the rich chemistry of silicon based aromatic compounds. The possibility of depositing such molecules on bulk silicon substrates should lead to devices which can be easily integrated into existing silicon microstructures and should show superior performance under ambient conditions. Such a rational design of new materials based on molecular properties should generate excitement in the evolving area of molecular materials. A deeper understanding of the basic forces between the substrate and the molecules can minimize dissipation channels in the charge separation processes and would further augment the discovery of new phases of in two-dimensional silicon physics. Clearly, such systems provide

a possibility of synergy between chemical synthesis, computational materials design and exotic physical properties.

**Acknowledgements** The authors are thankful to long-term discussions in the area of molecular vibrations in silicon systems to Alexander Boldyrev, Issac B. Bersuker and G. Narahari Sastry. Funding from INSA, DST, BRNS is duly acknowledged. Computational resources of the IACS-CRAY supercomputer for many of the calculations is highly appreciated.

## References

1. M. Sainsbury, *Aromatic Chemistry* (Oxford Science Publications, Oxford, 1992)
2. E. Hückel, *Z. Physik* **72**, 310 (1931)
3. E. Hückel, *Z. Physik* **70**, 204 (1931)
4. E. Hückel, *Z. Physik* **76**, 628 (1932)
5. J. Cai, P. Ruffieux, R. Jaafar, M. Bieri, T. Braun, S. Blankenburg, M. Muoth, A.P. Seitsonen, M. Saleh, X. Feng, K. Mullen, R. Fasel, *Nature* **466**, 470 (2010)
6. K. Wakita, N. Tokitoh, R. Okazaki, S. Nagase, *Angew. Chem. Int. Ed.* **39**, 634 (2000)
7. N. Tokitoh, K. Wakita, R. Okazaki, S. Nagase, P. von Ragué Schleyer, H. Jiao, *J. Am. Chem. Soc.* **119**, 6951 (1997)
8. P. Jutzi, M. Meyer, H.V.R. Dias, P.P. Power, *J. Am. Chem. Soc.* **112**, 4841 (1990)
9. N. Tokitoh, A. Shinohara, T. Matsumoto, T. Sasamori, N. Takeda, Y. Furukawa, *Organometallics* **26**, 4048 (2007)
10. Y. Tanabe, Y. Mizuhata, N. Tokitoh, *Organometallics* **29**, 721 (2010)
11. K. Abersfelder, A.J.P. White, H.S. Rzepa, D. Scheschkewitz, *Science* **327**, 564 (2010)
12. S. Nagase, H. Teramae, T. Kudo, *J. Chem. Phys.* **86**, 4513 (1987)
13. K.K. Baldrige, O. Uzan, J.M.L. Martin, *Organometallics* **19**, 1477 (2000)
14. S. Nagase, *Bull. Chem. Soc. Jpn* **87**, 167 (2014)
15. W.D. Hobey, *J. Chem. Phys.* **43**, 2187 (1965)
16. L. Blancafort, M.J. Bearpark, M.A. Robb, *Mol. Phys.* **104**, 2007 (2006)
17. I.B. Bersuker, *Chem. Rev.* **113**, 1351 (2013)
18. D. Jose, A. Datta, *J. Phys. Chem. C* **116**, 24639 (2012)
19. H. Şahin, S. Cahangirov, M. Topsakal, E. Bekaroglu, E. Akturk, R.T. Senger, S. Ciraci, *Phys. Rev. B* **80**, 155453 (2009)
20. G.G. Guzmán-Verri, L.C. Lew Yan Voon, *Phys. Rev. B* **76**, 075131 (2007)
21. I. Bersuker, *The Jahn-Teller Effect* (Cambridge University Press, 2006)
22. P. Garcia-Fernandez, I.B. Bersuker, J.E. Boggs, *J. Chem. Phys.* **124**, 044321 (2006)
23. H.J. Worner, F. Merkt, *J. Chem. Phys.* **127**, 034303 (2007)
24. Y. Liu, S. Kumari, M. Roudjane, S. Li, D.-S. Yang, *J. Chem. Phys.* **136**, 134310 (2012)
25. K. Pokhodnya, C. Olson, X. Dai, D.L. Schulz, P. Boudjouk, A.P. Sergeeva, A.I. Boldyrev, *J. Chem. Phys.* **134**, 014105 (2011)
26. A.P. Sergeeva, A.I. Boldyrev, *Organometallics* **29**, 3951 (2010)
27. T.R. Galeev, A.I. Boldyrev, *Phys. Chem. Chem. Phys.* **13**, 20549 (2011)
28. M. Houssa, G. Pourtois, V.V. Afanas'ev, A. Stesmans, *Appl. Phys. Lett.* **97**, 112106 (2010)
29. M. Ezawa, *New J. Phys.* **14**, 033003 (2012)
30. D. Jose, A. Datta, *Phys. Chem. Chem. Phys.* **13**, 7304 (2011)
31. Z. Slanina, *Chem. Phys. Lett.* **161**, 175 (1989)
32. C. Gerdes, T. Müller, *Angew. Chem. Int. Ed.* **49**, 4860 (2010)
33. T. Szilvási, T. Veszprémi, *Organometallics* **31**, 3207 (2012)
34. R.G. Pearson, *Proc. Natl. Acad. Sci.* **72**, 2104 (1975)
35. J.C. Ma, D.A. Dougherty, *Chem. Rev.* **97**, 1303 (1997)
36. D.A. Dougherty, *Science* **271**, 163 (1996)

37. C.A. Hunter, C.M.R. Low, C. Rotger, J.G. Vinter, C. Zonta, Proc. Natl. Acad. Sci. **99**, 4873 (2002)
38. S.E. Wheeler, K.N. Houk, J. Am. Chem. Soc. **131**, 3126 (2009)
39. S. Mecozzi, A.P. West, D.A. Dougherty, J. Am. Chem. Soc. **118**, 2307 (1996)
40. S. Tsuzuki, M. Yoshida, T. Uchimaru, M. Mikami, J. Phys. Chem. A **105**, 769 (2001)
41. A.D. Zdetsis, J. Chem. Phys. **127**, 214306 (2007)
42. S.A. Abraham, D. Jose, A. Datta, ChemPhysChem **13**, 695 (2012)
43. G.R. Hutchison, M.A. Ratner, T.J. Marks, J. Am. Chem. Soc. **127**, 2339 (2005)
44. J.-L. Brédas, D. Beljonne, V. Coropceanu, J. Cornil, Chem. Rev. **104**, 4971 (2004)
45. O. Marra, C. William, *Handbook of Semiconductor Silicon Technology* (1990)
46. S.F. Boys, F. Bernardi, Mol. Phys. **19**, 553 (1970)
47. J. Huang, M. Kertesz, J. Chem. Phys. **122**, 234707 (2005)
48. A. Datta, S. Mohakud, S.K. Pati, J. Mater. Chem. **17**, 1933 (2007)
49. A. Datta, S. Mohakud, S.K. Pati, J. Chem. Phys. **126**, 144710 (2007)
50. D.C. Elias, R.R. Nair, T.M.G. Mohiuddin, S.V. Morozov, P. Blake, M.P. Halsall, A.C. Ferrari, D.W. Boukhvalov, M.I. Katsnelson, A.K. Geim, K.S. Novoselov, Science **323**, 610 (2009)
51. J.O. Sofo, A.S. Chaudhari, G.D. Barber, Phys. Rev. B **75**, 153401 (2007)
52. M. Hu, X. Zhang, D. Poulidakos, Phys. Rev. B **87**, 195417 (2013)
53. J. Lan, D. Cheng, D. Cao, W. Wang, J. Phys. Chem. C **112**, 5598 (2008)
54. J.P. Lowe, K.A. Peterson, *Quantum Chemistry*, 3rd edn. (Elsevier, USA, 2006)
55. A.C. Ferrari, J.C. Meyer, V. Scardaci, C. Casiraghi, M. Lazzeri, F. Mauri, S. Piscanec, D. Jiang, K.S. Novoselov, S. Roth, A.K. Geim, Phys. Rev. Lett. **97**, 187401 (2006)
56. A.C. Ferrari, Solid State Commun. **143**, 47 (2007)
57. E. Scalise, M. Houssa, G. Pourtois, B. Broek, V. Afanas'ev, A. Stesmans, Nano Res. **6**, 19 (2013)
58. E. Cinquanta, E. Scalise, D. Chiappe, C. Grazianetti, B.V.D. Broek, M. Houssa, M. Fanciulli, A. Molle, [arXiv:1212.5422](https://arxiv.org/abs/1212.5422) [cond-mat.mes-hall]
59. D. Jose, A. Nijamudheen, A. Datta, Phys. Chem. Chem. Phys. **15**, 8700 (2013)
60. P.J. Hay, W.R. Wadt, J. Chem. Phys. **82**, 299 (1985)
61. L.E. Roy, P.J. Hay, R.L. Martin, J. Chem. Theory Comput. **4**, 1029 (2008)
62. A.W. Ehlers, M. Böhme, S. Dapprich, A. Gobbi, A. Höllwarth, V. Jonas, K.F. Köhler, R. Stegmann, A. Veldkamp, G. Frenking, Chem. Phys. Lett. **208**, 111 (1993)
63. D. Feller, J. Comput. Chem. **17**, 1571 (1996)
64. K.L. Schuchardt, B.T. Didier, T. Elsethagen, L. Sun, V. Gurumoorthi, J. Chase, J. Li, T.L. Windus, J. Chem. Inf. Model. **47**, 1045 (2007)
65. M. Moskovits, Rev. Mod. Phys. **57**, 783 (1985)
66. K. Kneipp, H. Kneipp, I. Itzkan, R.R. Dasari, M.S. Feld, Chem. Rev. **99**, 2957 (1999)
67. S.E.J. Bell, N.M.S. Sirimuthu, Chem. Soc. Rev. **37**, 1012 (2008)
68. R.M. Stöckle, Y.D. Suh, V. Deckert, R. Zenobi, Chem. Phys. Lett. **318**, 131 (2000)
69. E. Bailo, V. Deckert, Chem. Soc. Rev. **37**, 921 (2008)