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Poznań, April 27, 2025

REVIEW

of the doctoral thesis by **Mr. Elavenil Ganesan**, entitled:
"Photochemistry and Spectroscopy of Small, Cryogenically Isolated Organopnictogen Molecules"

Formal Basis for Evaluation

This review has been prepared in accordance with the resolution of the Scientific Council of the Institute of Physical Chemistry, Polish Academy of Sciences (IChF PAN), dated 25 February 2025, appointing me as the reviewer in the proceedings for awarding the degree of Doctor of Philosophy (PhD) to Mr. Elavenil Ganesan, M.Sc. The submitted doctoral thesis is written in English and bears the title: *"Photochemistry and Spectroscopy of Small, Cryogenically Isolated Organopnictogen Molecules."* I was officially informed of the Council's decision by Prof. Jacek Gregorowicz, Deputy Director for Scientific Affairs at IChF PAN. All documents related to the review process were provided to me electronically, followed by a hard copy, by Ms. Agnieszka Pietrzyk-Le from the Scientific Secretariat of IChF PAN by email on 3 March 2025.

This review has been carried out in accordance with Article 187 of the Act of 20 July 2018 – Law on Higher Education and Science (Journal of Laws of 2024, item 1571, as amended). I have also adhered to the terms of the agreement between the Institute of Physical Chemistry, Polish Academy of Sciences, and myself regarding the preparation of this review. My assessment is based on my own expertise while also referencing universal principles of academic tradition and scholarly practice.

Documentation submitted

The attached materials include, among others:

- The doctoral thesis (in English),
- A one-page abstract in English,
- A one-page summary in Polish.

The documents have been prepared in a clear and meticulous manner, allowing for a thorough evaluation of the thesis, particularly in assessing the scientific achievements that form the basis of Mr. Elavenil Ganesan's doctoral dissertation.

Formal Structure and Composition of the Doctoral Thesis

The dissertation by Mr. Elavenil Ganesan, titled "Photochemistry and Spectroscopy of Small, Cryogenically Isolated Organopnictogen Molecules", presents a meticulously structured and comprehensive exploration of the photochemical behaviour and spectroscopic properties of organopnictogen compounds under cryogenic conditions. The work adheres to rigorous academic standards, balancing

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theoretical foundations, experimental methodologies, and detailed analytical discussions.

Organisation and flow

The thesis opens with essential preliminary sections, including acknowledgements, funding declarations, and lists of publications and presentations, which contextualise the research within the broader academic and institutional framework. A bilingual abstract written in English and Polish (Streszczenie) ensures accessibility to international and Polish-speaking audiences, reflecting the formal requirements.

The introductory chapter establishes the scientific background, clearly defining key concepts such as pnictogens, matrix isolation techniques, and the principles of infrared and electronic spectroscopy. It also outlines the study's objectives, emphasising the novelty of investigating small, cryogenically trapped organopnictogen molecules—a niche, yet significant area in physical chemistry.

Subsequent chapters transition seamlessly from methodological foundations to experimental and analytical results. The second chapter provides a detailed description of the materials, tools, and procedures, including cryogenic sample preparation, photolytic radiation sources, and spectroscopic techniques. This section is particularly noteworthy for its transparency that allows reproducibility, a hallmark of robust scientific work.

The core analytical chapters (3–6) present the photochemistry and spectroscopy of specific compounds, each structured to first review the existing literature before presenting original findings. For example, the study of phosphaethyne (HCP) and the phosphaethynyl radical (CP) combines infrared spectroscopy with luminescence analysis, offering insight into the radical's phosphorescence behaviour, a rare phenomenon for such species. Similarly, the comparative analysis of methylpnictines (CH_3XH_2; X = P, As, Sb) systematically explores their photolytic fragmentation pathways, highlighting both common trends and element-specific reactivity.

A dedicated chapter on ethynylstibinidene (HCCSb) and ethynylarsinidene (HCCAs) stands out for its focus on the electronic spectroscopy and luminescence of these radicals, bridging the gap between matrix isolation studies and potential astrochemical applications. The investigation of propadienylphosphine (CH_2=C=CH-PH_2) further enriches the discussion by examining wavelength-dependent photolysis mechanisms, underscoring the interplay between molecular structure and reactivity.

The concluding chapter effectively synthesises the findings, revisiting the original objectives and proposing future research directions. The author's ability to connect disparate experimental observations into a cohesive narrative speaks to the intellectual rigour and depth of the thesis.

Supplementary Materials and Scholarly Rigour

The thesis is supported by an extensive reference list citing both foundational and contemporary works, demonstrating the author's involvement with the broader scientific literature. The appendices provide additional technical details, such as the specifications of cryogenic equipment and computational data, enhancing the transparency of the work.

Visual aids, figures and tables, are thoughtfully integrated, presenting spectral data, reaction schemes, and computational results with clarity. Their systematic listing at the end of the thesis ensures easy navigation.

Stylistic and Formal Compliance
Written in clear academic English, the thesis maintains a consistent tone and logical progression. The inclusion of a Polish summary aligns with institutional norms, while the adherence to IUPAC nomenclature and standardised units reflects the author's attention to detail.

Overall impression
This dissertation exemplifies a model of scholarly writing that combines methodological precision with analytical depth. Its well-defined structure, from foundational theory to cutting-edge experimental results, not only advances the understanding of organopnictogen chemistry but also serves as a valuable reference for future studies in cryogenic photochemistry and molecular spectroscopy.

Notes on content for the dissertation. Questions and comments
Chapter 1: Introduction
The reviewer appreciates how the chapter seamlessly bridges astrochemistry, spectroscopy, and quantum mechanics, offering a compelling rationale for studying heavier pnictogens. The good point is to see how the author contextualises the research gap: While phosphorus chemistry is well-explored, arsenic and antimony remain underexamined despite their potential roles in prebiotic chemistry. The discussion on interstellar molecule detection (e.g., CP, AsH_3) is particularly engaging, though a question arises: Are there newer detections of these species that could further strengthen the astrochemical motivation? The choice of HCCP, HCCA, and HCCSb as focal molecules is intriguing, but the reviewer wonders: What specific properties of these triple-bonded systems make them ideal for this study? *A brief justification would help the reader to appreciate their significance.* In my personal opinion, this chapter is the weakest of the entire dissertation. Sometimes the mental shortcuts, the definitions provided, and the short treatment of the introduction are a bit irritating and contrast with the following chapters, which are full of information, their good presentation and discussion.
Chapter 2: Methodology
The reviewer appreciates details in describing experimental protocols, from HCP synthesis to matrix isolation conditions. It is commendable to see how the author addresses potential pitfalls, such as the reactivity of precursors such as $CHCl_2$-PH_2. That said, a practical question emerges: *Could DBU, as a strong base, introduce interfering byproducts, and were these ruled out experimentally?* The computational methodology is robust, though one might ask: **Was B3LYP selected after benchmarking against other functionals, especially for excited states where some hybrid methods might perform better?** The reviewer also notes that while argon matrices are standard, neon could offer sharper bands, and were trade-offs between cost and resolution considered?
Chapter 3: Phosphaethyne (HCP) and Radical Phosphaethynyl (CP)
Here, the thesis delivers a notable achievement: the first observation of CP phosphorescence, a rarity for small radicals. The reviewer finds the intersystem crossing mechanism particularly compelling, especially with supporting DFT calculations. However, a natural follow-up question arises: Could other photoproducts, like the HPC isomer, form transients but evade detection because of

low concentrations? The luminescence data are groundbreaking, but how might CP behaviour differ in neon or krypton matrices, where site effects could be minimised?
Chapter 4: Photochemistry of methylpnictines (CH_3XH_2, X = P, As, Sb)
The reviewer is struck by the elegant contrast in the photolysis pathways: While P and As favour dehydrogenation (resulting in CH_2 = XH), Sb uniquely cleaves its C–Sb bond to form the triplet CH_3Sb. The first IR spectra of CH_2=AsH and CH_3Sb are significant contributions, but this raises a puzzle: Why is CH_2=SbH conspicuously absent? *Is it inherently unstable or does it decompose too rapidly to observe?* The wavelength dependence is another highlight: *why does 254 nm light drive C–Sb cleavage for Sb but dehydrogenation for P/As?* The reviewer suggests that multireference calculations (eg CASSCF) could further clarify the triplet-state dynamics of CH_3Sb.
Chapter 5: Ethynylstibinidene (HCCSb) and Ethynylarsinidene (HCCAs)
This chapter breaks new ground with the first spectroscopic detection of HCCSb, a feat that expands the family of ethynylpnictinidenes. The reviewer is fascinated by the luminescence signals, tentatively assigned to singlet→singlet transitions, though a critical question lingers: *Could triplet states also contribute, given the heavy-atom spin-orbit coupling in Sb/As?* The absence of the HCCSbH radical is puzzling: *Does photolysis proceed through a concerted H_2 loss, or is the radical too short-lived?* The reviewer notes that spin-orbit effects, though omitted here, might be a key to understanding these systems fully.
Chapter 6: Photochemistry of Propadienylphosphine (CH_2=C=CH-PH_2)
The discovery of phosphabutadiyne (HC_3P), a phosphorus analogue of interstellar HC_3N, is a highlight. The reviewer appreciates the wavelength-dependent selectivity: The VUV light cleanly produces HC_3P, while the UV light produces fragmentation. Yet, a mechanistic question appears: *Is H_2C=CH-CP a direct precursor to HC_3P, or are there hidden intermediates?* Are these too unstable or are their bands masked by noise? The reviewer suggests that time-resolved IR could help track these elusive species.
Chapter 7: Conclusions and future prospects
The reviewer sees the ambitious scope of the thesis, from astrochemistry to excited-state dynamics. The proposal to search for HC_3P in space is especially exciting, given its newly measured spectra. However, a lingering thought emerges: *The emphasis on spin-orbit effects in future work is appropriate; however, would high-resolution luminescence studies resolve the current ambiguities in the assignments of HCCSb?*

Overall Assessment and Conclusions

The thesis represents a significant contribution to pnictogen chemistry, featuring important and remarkable discoveries in the spectroscopy and photochemistry of heavy elements of Group 15. Although some mechanistic details require further exploration, as natural as possible, the work establishes a rigorous foundation for future research.

Formal recommendation

According to Article 187 of the Act of 20 July 2018 – The Law on Higher Education and Science (Journal of Laws 2024, item 1571, as amended), and based on this review of the doctoral dissertation "Photochemistry and Spectroscopy of Small,

Cryogenically Isolated Organopnictogen Molecules", I recommend admitting Mr. Elavenil Ganesan, M.Sc., to the subsequent stages of the doctoral procedure. Furthermore, I propose that the dissertation be awarded a distinction in recognition of its high quality.

Prof. Marek Sikorski

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Dokument podpisany przez Marek Sikorski
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