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REVIEW

of the doctoral dissertation entitled:

"Photochemistry and spectroscopy of small, cryogenically isolated organopnictogen molecules"

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The presented dissertation focuses on spectroscopic and photochemical properties of simple phosphorous-, arsenic-, and antimony-containing molecules of astrophysical importance. Many nitrogen-containing chemical compounds, potential precursors to large biomolecules, have been studied and widely detected in space. But only few phosphorous-bearing compounds have been identified in extraterrestrial environments and arsenic has been found in the form of AsH_3 in the atmospheres of Jupiter and Saturn. So, the photochemistry and spectroscopy of small oxygen-free molecules containing trivalent or monovalent pnictogen atoms heavier than nitrogen are a very current subject of research. In the presented dissertation the photochemistry of such species was investigated, starting from single-carbon molecules: phosphaethyne (HCP), methylphosphine (CH_3PH_2), methylarsine (CH_3AsH_2) and methylstibine (CH_3SbH_2). Next, two-carbon molecules: vinylarsine ($H_2CCHAsH_2$) and ethynylstibine ($HCCSbH_2$), together with the three-carbon molecule propadienylphosphine ($H_2CCCHPH_2$) were also studied. All these compounds (except HCP) represent the family of pnictines with XH_2 grouping, where $X = P, As, Sb$.

The specific objectives of the dissertation are:

- Photochemical studies of HCP in an argon matrix after its successful synthesis.
- Description of differences in methylpnictines photolyses as well as comparison with the reactions observed for methylamine and spectroscopic characterization of the respective photoproducts.

- Finding whether ethynylstibinidene, HCCSb, can be obtained in a rare gas matrix following the photodehydrogenation route already explored for ethynylarsinidene, HCCAs, and ethynylphosphinidene, HCCP, as well as spectroscopic characterization of ethynylstibinidene HCCSb, and the search for electronic luminescence of HCCSb, HCCAs, and HCCP.
- Obtaining phosphabutadiyne, HC_3P, by photodehydrogenation of a suitable precursor and also spectroscopic characterization of this phosphorous-bearing analogue of cyanoacetylene.

The doctoral thesis is written in a traditional manner, the layout is logical and clear. The thesis consists of 136 pages organized into 9 chapters and includes a list of 73 figures and a list of 38 tables. 201 bibliographic entries are cited.

The dissertation opens with a very short, 10-page Chapter 1, in which the Author only signals the issues within the area of his research. These are: basic properties of atoms of pnictogen group, infrared and electronic spectroscopy, photochemistry, examples of organic intermediates, a general description of matrix isolation technique. The chapter ends with a statement of the work objectives and a table containing a short list of precursors and plausible products of the photochemical reactions. Chapter 2 entitled *Materials, tools and procedures* is devoted to the description of sample preparation for studies in low temperature matrices, excitation sources, spectroscopic measurements, and calculation methodology. In this part, the Author, in his own way, briefly but comprehensively, describes all the procedures performed. The next chapters numbered 3 to 6 contain the results and discussion of the individual groups of photoproducts examined in this work.

Chapter 3 entitled *Phosphaethyne (HCP) and phosphaethynyl (CP) radical* provides new spectroscopic data on HCP. Full IR spectral characteristics of the molecule is presented together with identification of HCP-H_2O complex. At this point I would like to ask: (i) whether only one type of the mentioned complex is formed in the matrix, (ii) whether the Author has ruled out the formation of other structures, (iii) whether appropriate calculations have been performed. This is intriguing, especially since the observed distances between the bands for two HCP vibrations, created, as the Author claims, as a result of the matrix site effect, are relatively large: 24 cm^{-1} for ν_1 and 25 cm^{-1} for $2\nu_2$. The question arises whether such distances between the bands could be caused by weak interactions in a complex or in HCP aggregates. In this chapter one can find many very interesting and important results in the field of photochemistry. UV photolysis of HCP, monitored with both vibrational and electronic spectroscopy, revealed the CP radical as the only detectable product of irradiations, which enabled for the first time its spectroscopic investigations. Apart from the $B^2\Sigma^+$–$X^2\Sigma^+$ system detected in absorption, two $B^2\Sigma^+$–$X^2\Sigma^+$ and $B^2\Sigma^+$–$A^2\Pi_i$ fluorescence emissions were also studied. The phosphorescence of CP was discovered and explained by the new electronic systems: $a^4\Sigma^+$–$X^2\Sigma^+$ and $a^4\Sigma^+$–$A^2\Pi_i$. These unusual cases of quartet–doublet phosphorescence were analyzed, a plausible photophysical mechanism, suggested by theoretical studies, was also proposed, and all these achievements were published in an excellent journal Angewandte Chemie.

Chapter 4 entitled *Photochemistry of methylpnictines (CH_3XH_2, X = P, As, Sb)* focuses on explainig the photochemistry of methylphosphine, methylarsine and methylstibine in argon matrices and on the characterization of photolysis products with IR and UV/Vis spectroscopy. Photoproducts arising from CH_3PH_2 and CH_3AsH_2 are similar and include the P- and As-analogues of CH_2XH, HCX, CX, and XH, as well as CH_4. It was discovered that phosphaethene $CH_2{=}PH$ and arsaethene $CH_2{=}AsH$ could be further photolyzed using 254 nm radiation to produce HCX and hydrogen molecules. No CH_3-P or CH_3-As methylpnictinidenes were detected in these experiments and no evidence of the CH_3XH_2 isomeric species or isomers of the identified photoproducts was found. For methylstibine (CH_3SbH_2), the dehydrogenation channel produces only methylstibinidene, CH_3-Sb, an exotic compound of monovalent antimony. No evidence for an analogous CH_3-X product was found in photolyses of CH_3PH_2 or CH_3AsH_2. The cleavage of the C-Sb bond followed by formation of SbH and CH_4 proceeds more easily for Sb- than for the P- or As-analogues. The Author rightly notes that the photochemistry of methylphosphine and methylarsine in an argon matrix was found to be similar to the methylamine photochemistry, whereas methylstibine followed a different photochemical pathway. I have one comment here: when considering the formation of various photoproducts, did the Author consider the possibility of forming methane complexes with PH (phosphinidene), AsH or SbH in the matrix cage? Would that be possible?

Chapter 5 contains spectroscopic and photochemical studies carried out by the Author for ethynylstibine ($HCCSbH_2$) and vinylarsine ($H_2C{=}CH{-}AsH_2$). The most interesting part was the photolysis of ethynylstibine at 254 nm radiation that generated the photodehydrogenated photoproduct, triplet ethynylstibinidene (HCCSb). The Author rightly notes that together with earlier studies on HCCN, HCCP, and HCCAs, spectroscopic results obtained for HCCSb indicate that as the pnictogen atom mass increases in the series, the acetylenic-pnictinidenic electronic structure becomes dominant. In addition to HCCSb, three photoproducts: HCCH, SbH, and CCSb were observed after irradiation. Moreover, performed luminescence studies revealed electronic emission for both HCCSb and HCCAs, which was attributed to the radiative relaxation between two singlet excited states. I agree with the Author that further experimental and theoretical studies are needed to confirm this assignment.

In Chapter 6 photochemistry of propadienylphosphine ($CH_2{=}C{=}CH{-}PH_2$) in solid argon is described. First, a full infrared spectroscopic characterization of propadienylphosphine, 1, was obtained and the presence of two other isomeric species: propargylphosphine ($HCCCH_2PH_2$, 2) and propynylphosphine (CH_3CCPH_2, 3) was demonstrated with the relative concentration of all three isomers estimated at 85, 10 and 5% for isomers 1, 2 and 3, respectively. Next, the 254-nm photolysis of the C_3H_5P isomers generated several photoproducts (H–C≡C–C≡P, H_2C=CH–C≡P, H–C≡P, H–C≡C–H, H–C≡C–P, CH_4) and increased the concentration of propargylphosphine, 2. In turn, vacuum-UV photolysis decreased the amount of all three initial species and produced phosphabutadiyne, H–C≡C–C≡P, as the main photoproduct. Vinylphosphaethyne, (H_2C=CH–C≡P), the presence of which was detected in the matrix, was considered a reliable source of phosphabutadiyne. It is worth emphasizing that the results described in this chapter for propadienylphosphine are clearly consistent with those published for phosphabutyne (Lawzer et al., Phys. Chem. Chem. Phys. 2025), which was shown by the Author as a comparison of the corresponding photochemical reactions. At this point in the reviewed doctoral thesis I am left wondering about two things: i) did the Author consider the possibility of forming methane complexes with ethynylphosphinidene (HCCP) in the matrix cage? ii) since the Author identified phosphaethyne (HCP) and acetylene bands (page 89), why did he not assign them to the HCP-acetylene complex formed in the Ar matrix cage, especially since the same complex was described in detail in the mentioned publication?

In the last chapter of the work (Chapter 7) the Author presented conclusions from the conducted research and future outlook. It should be recognized that the conclusions are formulated correctly and reflect the results obtained in the work.

I consider the above description of the content of Mr. Ganesan's doctoral dissertation as an argument proving that this work contains many valuable experimental results, and their interpretation was made on the basis of performed theoretical calculations. The results on the properties of the studied molecules and the processes occurring after irradiation are valuable and significantly expand knowledge in the field of physical chemistry and even in the field of astrochemistry. Therefore, I assess the entire dissertation very well. I have no serious objections to the content of the dissertation, and below I am including only minor comments that are irrelevant to my positive assessment of the dissertation expressed above, because they do not undermine either the PhD student's reasoning or the conclusions he drew. Minor comments:

1) I did not find a description of how to introduce individual compounds into the matrix, the detailed description on page 13 only applies to phosphaethyne (HCP), and what about the others? How were the vapors of these substances obtained?
2) no unit on the Absorbance axis in most of the presented spectra,
3) incorrect signature of Figures 3-6, 3-7: is *Luminescence of CP in solid argon*, should be Luminescence spectrum of CP in solid argon; luminescence is a phenomenon, and the graph is a spectrum; Figure 5-4: is *Experimental and TD-DFT-predicted UV absorption of ethynylstibine*, should be Experimental and TD-DFT-predicted UV absorption spectra of ethynylstibine, similarly in Figures 5-9, 5-11, 5-16,

4) using both terms *frequency* and *wavenumber* for quantities expressed in cm^{-1},
5) titling of tables containing band wavenumbers: *Infrared spectroscopy of...*; IR spectroscopy is a measurement method (tables in Chapter 5 and 6),
6) what is meant by *"net effect"* in the spectra captions, e.g. in Figure 4-3, 4-12, etc.
7) how was the *normalization of concentrations* performed on the graphs of kinetic courses as a function of exposure time, Figures 4-8, 4-11, 5-5, 6-7?
8) in the work the words *"parent/parents/parent compound"* appear in the meaning of the precursor molecule, in my opinion this is not correct, because in organic chemistry it means the simplest member of a class of compounds from which derivatives may be obtained; the names of the parent structures are used in IUPAC nomenclature as the basis for systematic names,
9) presentation of calculated wavenumbers in different tables with different accuracy, e.g. Tables 5-1, 6-1, 9-2, 9-4, etc.
10) no information on the scaling factors of calculated wavenumbers, except for a few tables in Chapter 4,
11) in the list of references, two of them were repeated (Cho, Andrews 2012).

To sum up:

I assess the doctoral dissertation of Elavenil Ganesan, M.Sc. very well because the obtained results have great cognitive value, and some of them have already been published. The research, the results of which are included in the dissertation, was carried out carefully, the conclusions were well justified and the assumed goals of the work have been achieved. The performed experiments constitute a coherent whole, and the observed effects are very interesting. Positively assessing the doctoral dissertation of Elavenil Ganesan, M.Sc., I state that the thesis meets the requirements for doctoral dissertations as set out in the Law on Higher Education and Science of 20 July 2018 (as amended). I therefore request that the dissertation be accepted by the Scientific Council of the Institute of Physical Chemistry of the Polish Academy of Sciences and that Elavenil Ganesan, M.Sc. can be admitted to the further stages of the doctoral procedure. In addition, due to the amount of research material collected by the PhD student and the thorough and careful analysis of this material as well as the demonstrated knowledge of both experimental techniques and computational methods of quantum chemistry and taking into account the importance of the presented research for the development of astrochemistry, I request that the doctoral dissertation submitted for assessment be distinguished.

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