Skoltech
Skolkovo Institute of Science and Technology

Jury Member Report – Doctor of Philosophy thesis.

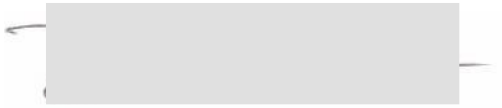
Name of Candidate: Iosif Leibin

PhD Program: Materials Science and Engineering

Title of Thesis: Spectra and mobility of open-shell atoms in rare gas crystals: effects of interaction anisotropy

Supervisors: Prof. Alexei Buchachenko, Asst. Prof. Aksenov Dmitry

Name of the Reviewer: David T. Anderson

I confirm the absence of any conflict of interest  (Alternatively, Reviewer can formulate a possible conflict)	**08/24/2024** **Date: DD-MM-YYYY**

The purpose of this report is to obtain an independent review from the members of PhD defense Jury before the thesis defense. The members of PhD defense Jury are asked to submit signed copy of the report at least 30 days prior the thesis defense. The Reviewers are asked to bring a copy of the completed report to the thesis defense and to discuss the contents of each report with each other before the thesis defense.

If the reviewers have any queries about the thesis which they wish to raise in advance, please contact the Chair of the Jury.

Reviewer's Report

Reviewers report should contain the following items:

- Brief evaluation of the thesis quality and overall structure of the dissertation.
- The relevance of the topic of dissertation work to its actual content
- The relevance of the methods used in the dissertation
- The scientific significance of the results obtained and their compliance with the international level and current state of the art
- The relevance of the obtained results to applications (if applicable)
- The quality of publications

The summary of issues to be addressed before/during the thesis defense

This thesis describes theoretical work on predicting the trapping sites and potential migration pathways of open-shell atoms in rare gas crystals which is needed in the interpretation of matrix isolation experiments. Matrix isolation spectroscopy is a method used to characterize highly reactive species, such as atoms with unpaired electrons, by trapping them in a chemically inert matrix of rare gas atoms at very low temperature to prevent reaction and permit the atomic species to be studied spectroscopically (ESR, infrared, Raman, and UV/Vis). Theoretical predictions of the trapping site geometry and its symmetry can be used to assign the observed atomic spectra to specific trapping sites. Calculation of the barriers and pathways for diffusion of the atom inside the bulk rare gas solid are needed to better design and interpret thermally induced diffusion experiments aimed at studying the low temperature reactivity of the atom. In my opinion what distinguishes this work from other theoretical work in this area is that the open-shell nature of the atom is explicitly incorporated into the intermolecular potential between the guest atom and rare gas host. This is non-trivial for open shell atoms, and the thesis shows that this level of accuracy is necessary to fully interpret many matrix isolation experiments. The dissertation is well organized, starting with an extensive introduction and literature review, followed by Chapter 3 which describes the methodology in detail, and finally in Chapter 4 the results of several projects are reported. I also liked that the student listed his four publications that have come out of this thesis work on page 3 of the thesis; he lists four papers all published in high quality physical chemistry journals.

As discussed in the thesis, matrix isolation spectroscopy is a mature research field and thus to make new contributions requires improvement in the theoretical modeling. In many cases the available experimental data on thermally-activated migration is scattered with discrepancies between different experiments, refinement of activation energies for different migration pathways is necessary to understand the specificity of low temperature reactions in different matrices, and the available experimental information permits rigorous comparison between experiment and theory in many cases. Finally, with the many advancements in computing power, these types of studies were not possible 20 years ago.

The computational methods used in this work are based on first principles. Explicit treatment of the open shell nature of the atom's interaction with the rare gas atoms is necessary to achieve the level of agreement with experiment presented in this thesis. Previous theoretical treatments usually approximate the intermolecular interaction as isotropic and neglect anisotropic terms in the intermolecular interaction. Obviously, treating this anisotropy makes the computations more complicated, but is necessary to find good agreement between experiment and theory. Specifically, the alternative formulation of the DIM method for P-state atoms that boosts computational efficiency is a significant advance in the theory.

The work on trapping and thermal migration of first- and second- row atoms in Ar, Kr, and Xe crystals is first rate, treating the anisotropic interactions with the crystal inherent to P-state atoms B, C, O and F. This is further demonstrated in the work on O(^{3}P) and C(^{3}P) where they demonstrate the profound effect of the angular momentum anisotropy in O(^{3}P) and make predictions for C(^{3}P). The thesis work is then extended to O(^{3}P) studies in order to examine the effect of spin-orbit coupling to make some of the most rigorous thermodynamics calculations to date on the accommodation and migration of ground state oxygen atoms in Ar, Kr, and Xe. Finally, the work on Ba atoms in Ar, Kr, and Xe matrices predicts a specific matrix site that is consistent with the available experimental data. This is first rate theoretical work on matrix isolation systems that can be modeled from first principles and compared with

experiment.

Our understanding of mass transport and accommodation of guest atoms in molecular crystals is fundamental to a variety of scientific fields, specifically astrochemistry and atmospheric science. This theoretical work is also fundamental to spectroscopy in condensed phases where gas phase selection rules are perturbed and altered in the condensed phase environment, and in the study of radiation induced chemical dynamics. There is also overlap with fundamental physics such as the Ba atom work which is involved in the search for neutrinoless double beta decay of Xe in the nEXO experiment.

The author reports four publications based on his thesis work in three different peer reviewed physical chemistry journals. All four publications are high quality and demonstrate a breadth of work related to atoms in rare gas matrices.

In summary, this thesis work represents high quality theoretical work on the trapping and migration of open shell atoms in rare gas matrices. Rare gas solids are ideal condensed phase model systems that require high level computational techniques to make rigorous comparisons to experiments. My only criticism is the numerous misspellings and typos that exist in the thesis in its current form, but I imagine that this can be cleared up quickly. The research documented in this thesis demonstrates a high level of skill and execution that makes the candidate worthy of defending his PhD and I look forward to the defense.

Provisional Recommendation

☒ *I recommend that the candidate should defend the thesis by means of a formal thesis defense*

☐ *I recommend that the candidate should defend the thesis by means of a formal thesis defense only after appropriate changes would be introduced in candidate's thesis according to the recommendations of the present report*

☐ *The thesis is not acceptable and I recommend that the candidate be exempt from the formal thesis defense*