Faculty of Chemistry
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Recenzja rozprawy doktorskiej mgr Sangami Ganesan Santhi

Report on Doctoral Thesis of MSc Sangami Ganesan Santhi

The PhD Thesis presented by MSc Sangami Ganesan-Santhi, under the title "Interactions and cold collisions involving AlF molecules" represents high quality, state-of the-art original research work.

The Thesis focuses on the theoretical studies representing necessary background for further developments of new methodologies for cooling mechanism in molecules, in particular the ones involving aluminium monofluoride (AlF) such as interactions with AlF itself or with Helium/Rubidium atoms, which are very promising candidates for producing ultracold degenerate dipolar gases. For that purpose highly accurate potential energy surfaces (PES) are developed based on the Coupled Cluster (CC) and Multi Reference Configuration Interaction (MRCI) approaches taking into account also the basis set convergence and relativistic effects. These PES involving ground and excited states of AlF and related tri-and tetra atomic systems, have been in most cases developed for the first time, at higher dimensionality or higher level of theory. Moreover, PhD Thesis includes also scattering calculations for AlF-He system, which directly provided insights to the buffer gas cooling process.

This PhD Thesis represents an interdisciplinary approach joining quantum mechanical theory and scattering calculations for the accurate prediction of spectroscopic properties and physical processes in ultracold molecules, which are necessary to guide experimental studies on ultracold matter.

The Thesis, a well written and structured work, which consists of eight chapters, begins with an overview in the Introduction. This first chapter briefly describes the aspects related to quantum behavior in ultracold regime, starting from the historical perspective on predictions of Bose-Einstein condensate, followed by its first realization in 1995, towards more recent topics on emerging applications of ultracold molecules. This chapter includes also an overview of different methodologies allowing production of cold molecules, discussing molecule-specific aspects such as vibrational states and Franck-Condon factors governing transitions between them. Next, more details on the aim of the research, theoretical investigation on the feasibility of aluminium monofluoride cooling, are presented describing its advantages due to highly diagonal Frank-Condon factors, chemical stability, and large dipole moment; followed by the discussion on its presence in the Interstellar Medium (ISM) and other relevant prior studies.

Third chapter describes the theoretical background, with a particular focus on ab initio electronic structure calculations and scattering theory. Starting from Born-Oppenheimer approximation, Hartree-Fock method, Basis Sets and its complete limit, more advanced electronic structure methodologies accounting for electron correlation and relativistic effects allowing single or multireference computations in the ground and excited

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electronic states are introduced and briefly described. This part is followed by the overview of scattering theory and quantities relevant to this study.
Chapters four to seven present results on the AlF, and binary systems AlF-He, AlF-AlF and AlF-Rb. The AlF system is applied to discuss convergence of energy profiles and other parameters computed at different levels of theory with increasing basis sets. In this respect the ground state case stand as a benchmark to establish methodology applied also for the excited state study. In the fifth chapter results on AlF-He interaction are presented and applied to predict the buffer gas cooling prospect of AlF molecule. In this part multiple PES are derived for systems composed of AlF molecule in the ground and several excited states in conjunction with ground state He atom. Comparison among applied ab initio methodologies is extended to explicitly correlated approaches and basis sets, discussing both accuracy and computational cost. These computations provide crucial information on the nature of global and local minima, while PES are next used for collision dynamics simulations. The latter are performed within both elastic and inelastic regimes, with the high ratio of the former suggesting that buffer gas cooling of AlF molecule can be efficient. Chapter six discusses AlF-AlF system, increasing dimensionality of the problem, with full 4D-PES described by four parameters related to relative distance between two rigid AlF molecules and three angles describing their relative orientation. Furthermore computations beyond rigid rotor approximation are also performed for selected 1-D cuts of PES. All these computations are also performed for several electronic states with different multiplicities, providing very detailed analysis. In the last part of results AlF-Rb system is included, to study the possibility of sympathetic cooling of AlF molecules and observing magnetic Feshbach resonances in this system. Interaction energies are computed for the five states showing some similarities with those obtained for AlF-He.
Summary and outlook are gathered in the last, eight chapter highlighting different aspects related to development of accurate potential energy surfaces and performing efficient ab initio electronic structure calculation for a particular system. Moreover, based on the ab initio study of AlF-He interaction and scattering, the underlying mechanisms for cooling AlF, suggesting the great prospects for buffer gas cooling of AlF molecule, are considered important outcome of this Thesis. Overall all results presented in the PhD Thesis are of high quality, represent the value on its own as important starting point to understand the nature of AlF interactions as well as can be used further in scattering calculations or benchmarking less expensive methodologies.
In summary, the Thesis represents an extensive, high quality original research work, highly relevant from the methodological point of view, and due to providing important information for better understanding and prediction of cooling processes in ultracold matter. The Thesis is well and clearly written, with only some typographical errors, sometimes related to processing of references. In plus I would like to mention large number of clearly designed and informative figures, as well as an extensive and up-to-date bibliography with over 250 references.
In conclusion, I **evaluate positively** the Doctoral Thesis of MSc. Sangami Ganesan Santhi. In my opinion, the dissertation meets all statutory requirements showing overall good knowledge of PhD candidate in Physical Sciences as well as original contribution

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to the challenging and innovative research related to theoretical studies on interactions and cold collisions of AlF, molecules of importance for ultracold studies.

Podsumowując, **oceniam pozytywnie** rozprawę doktorską mgr Sangami Ganesan Santhi, która w pełni spełnia warunki wymagane do nadania stopnia doktora na Uniwersytecie Warszawskim, w szczególności:
1. Rozprawa doktorska prezentuje ogólną wiedzę teoretyczną kandydata w Dyscyplinie Nauki Fizyczne oraz umiejętność samodzielnego prowadzenia pracy naukowej.
2. Przedmiotem rozprawy doktorskiej jest oryginalne rozwiązanie problemu naukowego związanego z nowatorskimi badaniami teoretycznymi oddziaływań i zderzeń AlF, cząsteczki o istotnym znaczeniu w badaniach ultrazimnej materii.

Z poważaniem,

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