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Review of the PhD Thesis

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Affiliation:	Faculty of Physics, Institute of Physics, Astronomy and Informatics, Nicolaus Copernicus University in Toruń
Title of the thesis:	**Collision-induced line-shape effects in molecular spectra**
Supervisor:	dr. hab. Piotr Wcisło, prof. NCU

Introduction

The dissertation under review, prepared by PhD candidate mgr. Nikodem Stolarczyk, consists of **eight thematically matched** articles and labelled with the letters [A] – [H]. All articles have been published in the years 2021 - 2024 in renowned and refereed journals with high values of the impact factors: *Journal of Quantitative Spectroscopy and Radiative Transfer* – 5 papers, *The Journal of Chemical Physics* – 1 paper, *Physical Review A* – 1 paper and *Astronomy & Astrophysics* – 1 paper. The collection of the papers has been also supplemented with short Abstracts, Introduction and a section Author contribution statement – reporting the individual contribution of the author to each paper. The comparison of the content recently mentioned document with the declarations of the other co-authors (section Co-author contribution statements) clearly prove that there is no conflict of interest between all co-authors of the publications constituting the evaluated dissertation. Mr. Nikodem Stolarczyk is the first and corresponding author in the three papers (articles [A], [G] and [H]), the second one in next three (articles [B], [D] and [E]), while he is mentioned in further places in the publications [C] and [F].

Assessment

The main goal of the dissertation presented by Mr. Nikodem Stolarczyk is to derive a highly-accurate profiles of the rovibrational or pure rotational molecular lines from first principles. The continuous development of *ab initio* methods based on quantum scattering calculations is steel motivated by the significant development of the laser-based spectroscopic techniques, especially when applied to simple diatomic molecules with great astrophysical importance e.g. isotopologues of H_2 and CO. An accurate analysis of experimental spectra requires an accurate modelling of the spectral line-shape, beyond the Voigt profile.

The subject of the studies contained in the presented thesis can be divided into two main issues.

* I have no doubt, that Mr. Nikodem Stolarczyk is the one and only author of the presented dissertation despite of the typographical error in the first name of the author that is presented on the title page of the .pdf version of the thesis.

The first part is devoted to extending the methodology of simulating the spectral line profiles using parameters obtained from *ab initio* quantum scattering calculations for a few molecular systems, including H_2-Ar [A], CO-Ar [B], H_2-He [C, F], HD-He [D], HD-H_2[E], HD-He [D]. The standard and similar calculation procedure applied in articles [A] – [F] contains the determination of the six line-shape parameters representing the: collisional broadening and shift, the speed dependences of the broadening and shift parameters and Dicke narrowing – described by the complex Dicke parameter. Modeling of the spectral profiles was also based on the theoretical potential energy surfaces (PESs) and appropriate model of the collisions. In the next step, the applied methodology of calculation was validated by the comparison of the simulated spectra with the highly-accurate experimental spectra [A, B, E, F]. Moreover, the temperature dependence of the line-shape parameters under consideration have been described in the wide range of temperature [B-E] using the double-power-law (DPL) representation consistent with HITRAN database.

This part of the thesis contains a number of valuable results. It is enough to describe shortly the achievements obtained by the PhD candidate and co-workers in work [A], in which the contribution of the Mr Nikodem Stolarczyk was dominate:

- *ab initio* profile reproduced the experimental measurements of the S(1) 3-0 line of H_2 perturbed by Ar with about 1.6% agreement,
- the several different approaches to the theoretical line-shape profiles have been considered to obtain above mentioned agreement,
- the inclusion only effect of the centrifugal distortion in a simplified manner (simple CD) reduces the error in the line-shape parameters to below 1% (with no additional numerical cost),
- the collisional shift parameter δ_0 is extremely sensitive to inaccuracies of the PES,
- the highly-accurate cavity ring down spectroscopy (CRDS) technique has been applied to measure S(1) 3-0 transition in molecular hydrogen perturbed by argon.

The second part of the thesis (articles [G] and [H] by Stolarczyk, Wcisło and Ciuryło) is devoted to the novel approach of the modelling of the collisional line-shapes in the regime of very frequent velocity-changing collisions i.e. when the Dicke parameter being the dominant term. The work [G] demonstrates that speed-dependent hard-collision profile (SDHCP or SDNGP) collapse into a simple Lorentz profile. The analytical formulas for the effective width (Γ_{eff}) and shift (Δ_{eff}) of the Lorentzian were derived using quadratic approximation of the speed dependence of collisional width and shift. The limitation of using of the proposed approach to the systems in which perturber mass is comparable to absorber mass was removed in the next work [H]. The paper [H] generalized the mentioned above results using the billiard-ball (BB) model, which properly accounts the perturber-absorber mass ratio. The numerical validation of the derived Lorentz profile ($LP^{BB}(\alpha=2)$) with the speed-dependent billiard-ball profile (SDBBP($\alpha=2$)) for Q(1) 1-0 line in H_2 perturbed by He (see FIG. 3 of work [H]) clearly indicates the high value of the approach used by the authors. It should be noted that Mr. Stolarczyk was the leader of the "research project", which resulted in both articles [G] and [H].

The six articles [A - F] were caried out in cooperation with foreign research centres: University of Science and Technology of China (China), University of Rennes (France), Russian Academy of Sciences (Russia), University of Grenoble Alpes (France), Auburn University (USA), Tomsk State University (Russia) and Harvard-Smithsonian Center for Astrophysics, Atomic and Molecular Physics Division (USA). In my opinion, the cooperation with last institution, which maintains the HITRAN and HITEMP databases, is particularly important. The collaboration resulted in two of the presented publications [C, D], which provided a wide set of rovibrational lines for H_2 perturbed by He (3480 lines) and for HD

perturbed by He (11575 lines) at temperature between 20 and 1000 K. Both datasets are available as a part of the HITRAN database.

Moreover, Mr. Nikodem Stolarczyk published also five further articles which do not contribute directly to the presented thesis, but thematically relate to the similar issues i.e. calculations of the line-shape parameters and modeling the line profiles as well as the CRDS technique.

Summary and recommendation

Mr. Nikodem Stolarczyk has presented a vast body of work consisting of eight thematically matched articles in the field of theoretical molecular spectroscopy with detailed study of methodology for developing of highly-accurate spectral line profiles derived from first principles. The results obtained by the PhD candidate are surely of great interest and importance, also considering the possible applications in various fields, including quantitative molecular spectroscopy, optical metrology and studies of Earth and (exo)planet atmospheres.

I have no doubt that Mr. Nikodem Stolarczyk has presented important and valuable results dealing with methodology of simulating the molecular line profiles from the spectral line-shape parameters obtained through *ab initio* quantum scattering calculations.

Mr. Nikodem Stolarczyk has gained a broad understanding of vide aspects of the field under consideration and has mastered the typically employed theoretical methods very well. I am impressed with the amount of work, both computational and experimental, done within the framework of this dissertation - Mr. Nikodem Stolarczyk also performed the measurements of the D_2 lines perturbed by H_2 [E]. The reviewed thesis, especially articles [G] and [H] led by PhD candidate, proves that Mr. N. Stolarczyk has the ability to solve an important scientific problem and conduct independent research work.

Therefore, **I declare that the PhD thesis presented by Mr. Nikodem Stolarczyk meets all formal** (art. 187, p. 1 and 2, Act of 20 July 2018, Journal of Laws 2018, items 1668) **and customary requirements for the doctoral dissertations. I recommend the admission of Mr. Nikodem Stolarczyk to the further stages of the PhD procedure.** Moreover, I have found the thesis worthy of distinction due to the high importance of the conducted research and a large number of published articles constituting the current scientific achievements of the PhD candidate. A detailed justification of my recommendation is included in a separate document.

Wojciech Gajda