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Warszawa 23.07.2024

Review of the doctoral dissertation of Nikodem Stolarczyk, M.Sc.
"Collision-induced line-shape effects in molecular spectra".

The dissertation of Mr Nikodem Stolarczyk is devoted to modelling the shape of the spectral lines of the optical molecular resonances modified by collisions with atoms or molecules. In this dissertation, the line shape modelling is based solely on the results of theoretical calculations and its correctness is verified by comparison with experimental results. The high precision of modern measurement techniques and continuous progress in this field, causes that the Vigot profile in many cases turns out to be too simplified and does not allow reproduction of experimental data with the required accuracy. In the proper description of the line shape, it becomes necessary to take into account subtle effects, e.g. the influence of collisions of molecules changing their velocity, which leads to the Dicke narrowing, or the presence of correlations between collisions changing the state/phase and velocity of colliding atoms or molecules. Correct modelling of spectral line shapes is important not only for basic studies of interatomic interactions or collisions, but also for practical applications: measuring the concentration of greenhouse gases in the Earth's atmosphere or determination of the thermodynamic conditions of the atmosphere.

The presented dissertation is composed of eight thematically related scientific articles published in worldwide journals, preceded by a concise four-page introduction, and includes the authors' declarations of their contribution to these articles. In the presented dissertation, PhD student did not avoid minor errors, irrelevant from the point of view of scientific value, i.e. a typo in the name on the title page, incorrect publication citations on page 13, line 21 from the top - from the context it seems that it should be cited publication [C] and it is [A], while on line 22 from the top on this page it should be cited publication [D] and it is [B].

The publications included in the dissertation were published between 2021 and 2024 in the prestigious journals: Astronomy & Astrophysics (1 article), Physical Review A (1 article), Journal of Chemical Physics (1 article) and Journal of Quantitative Spectroscopy & Radiative Transfer (5 articles) and take up a total of 88 print pages in a similar format. All papers are co-authored (from 3 to 18 authors), in all of them one of the co-authors is the supervisor Dr. hab. Piotr Wcisło prof.-UMK apart from him, from the Institute of Physics of the Nicolaus Copernicus University and several co-authors from other research centres located in Poland, France, China, Russia, and USA.

The co-authors' statements of their contributions to the articles appended to the dissertation clearly indicate the individual contribution of Mr Nikodem Stolarczyk to the performed research and writing of the manuscripts. In three publications [A,G,H], Mr Nikodem Stolarczyk is a corresponding author, indicating that the he made a significant contribution to the creation of these papers. This is confirmed in the statements of the co-authors. In the works [G] and [H], the other two co-authors (Dr hab. P. Wcisło and Prof. Dr hab. R Ciuryło) pointed to a high degree of independence and a leading role of Mr Nikodem Stolarczyk both at the stage of performing the research and preparing the manuscript. They also emphasise that their role in the case of these two articles [G,H] was limited to mentoring and support in the development of the methodology used to derive analytical formulas for modelling the profile of spectral lines. According to the co-authors' statements, the PhD student also made a significant contribution to the paper [B] in which he is listed as the second author and first among the group of authors working on line shape modelling. In this paper he carried out calculations of spectral line shape parameters based on generalised spectroscopic effective cross sections, comparison of theoretical and experimental data. He also performed uncertainty analysis of the obtained results, and prepared the part of the manuscript describing these topics. In papers [C,D], the PhD student performed calculations of spectral line shape parameters based on generalised spectroscopic effective cross sections. He optimised the procedure of describing the line shape parameters using the double-power-law temperature dependence format. He presented line shape parameters using the above format for several thousand spectral lines. He also prepared parts of the manuscripts containing this information. It is also worth to emphases that apart from purely theoretical studies, Mr N. Stolarczyk carried out measurements of the shape of the rovibrational line S(2) 2-0 in the H_2 molecule modified by collisions with the D_2 molecule using a frequency-stabilised cavity ring-down spectrometer located at the Institute of Physics of the Nicolaus Copernicus University. The results of these measurements were used to validate the line shape calculation methodology in the paper [E]. The PhD student has co-authored a total of 13 scientific papers, which is a significant scientific output at such an early stage of his research career.

The first paper of the series [A], is devoted to the analysis of the effect on the rovibrational spectral line profile S(1) 3-0 of the H_2 molecule induced by collisions with Ar atoms. The work includes both an experimental part, in which the line profile of H_2 induced by collisions with Ar was determined by the CRDS technique for four different H_2:Ar partial pressures, and a theoretical part involving the modelling of line profiles using the Hesaa method based on quantum scattering *ab initio* calculations determined from potential energy surface of the H_2-Ar system. In this paper, several approximations were tested in the performed line profile calculations. The best agreement between the theoretical and experimental values was obtained for the parameters related to the line width, the least for the pressure shift. An analysis of the parameter uncertainties carried out by the PhD student showed that the main factor responsible for the discrepancy is the inaccuracy related to the determination of the potential energy surface of the H_2-Ar system.

In the paper [B], the rotational line profile of R(0) transition in CO molecule perturbed by collisions with Ar was modelled over a wide pressure range from 50 mTorr to 1500 Torr. The simulation results were compared with the profile of this line measured over this pressure range. A modified speed-dependent van Vleck-Weisskopf profile was used to simulate the line profiles in the high pressure range, while in the low pressure range a speed-dependent Voigt profile was used. An analysis of the calculation results has shown that the best agreement, at a sub-percentage level, of the synthetic spectral line profiles with the experimental one was obtained by including the effect of line mixing in the calculations. Calculations were carried out using two independent potential energy surfaces. In results similar agreement between synthetic and experimental line profile has been reported in both cases. Carefully chosen calculation conditions allow that the line shape and shift parameters can be determined with high accuracy over a wide temperature range.

The work [C] is dedicated to the complex modelling of profiles of a series of rovibrational lines of the H_2 molecule modified by collisions with H_2 molecules or He atoms. The paper addresses the problem of determining the line shapes available in the HITRAN database for a wide range of measurement conditions. In contrast to the method used so far, where the line shape parameters were determined from fitting a model to experimental data, it was proposed to determine these parameters from *ab initio* quantum-scattering calculations. From theoretical calculations, the line-shape parameters: broadening and shift, their speed dependence, and the complex Dicke parameter were determined for all H_2 spectral lines available in the HITRAN database. A validation of the modelling was carried out by comparing the values obtained with the data found in the HITRAN database. The line shape parameters obtained from the calculations were presented in the universal form in the double-power-law temperature dependent format, allowing relatively easy determinations of their values over a wide temperature range (from 20K to 1000K). In total, line shape parameters were determined for 3480 transitions in the H_2 molecule perturbed by collisions with He atoms. The same approach was used in the work [D], in which line shape parameters were determined for 11575 transitions in the HD molecule perturbed by collisions with He atoms, and the calculated values of the line shape parameters were presented in the double-power-law temperature dependent format and placed in the HITRAN database. In both cases the parameters published in the database allow for a relatively simple determination of the shape of the spectral lines using beyond-Voigt profile over a wide temperature range.

The manuscript [E] published in Astronomy & Astrophysics concentrates on the determination from first principles of collision line shape parameters in the context of astrophysical observations. It focuses on modelling the R(0), R(1) and R(2) line profiles of an HD molecule modified by collisions with He atoms or H_2 molecules. The modelling covers a wide range of temperatures and pressures, in particular covering the values of these parameters that may occur in the atmospheres of giant planets. The authors describe the calculation methodology and presents a simulation of the line-shapes with a modified Hartmann-Tran profile. The study reveals that for a correct description of the line shape it is necessary to use a model that takes into account collisional broadening and shift, their speed dependencies, and the complex Dicke effect. If these factors are not taken into account, the effective width and height of the spectral lines of the HD molecule will be falsified. As a result, this may lead to an erroneous determination of the thermodynamic conditions relevant to the atmospheres of giant planets (temperature, pressure, and gas composition).

The paper [F] describes a study of the effect of collisions between He atoms and a hydrogen molecule on the experimentally observed line-shape of the 3-0 S(1) and 2-0 Q(1) transitions in a hydrogen molecule. In this work it has been shown that in order to simulate from first principles the profile of these lines under the conditions in which the measurements were made, it is necessary to include collisional broadening and shift, their speed dependencies and the complex Dicke effect in the model. By including these effects in the calculations, a sub-percentage level of agreement was obtained between the line shapes recorded using cavity ring-down spectroscopy and the line profiles obtained from first-principles calculations.

The last two papers of the series [G,H] are devoted to the behaviour of the spectral lines in the regime of the frequent velocity-changing collisions. In these papers it was shown that under these conditions the complex line profiles (i.e., Hartman-Tran profile or quadratic speed-dependent hard collision profile or the billiard ball profile) can be approximated by the Lorentz profile. In the paper [G] it was shown that the speed-dependent hard collision profiles in the regime of frequent velocity changing collisions collapse to the Lorentz profile. The PhD student derived analytically formulas describing collisional broadening and shift in the Lorentz profile when perturber and absorber masses are comparable, while in the paper [H] he considered the case when perturber and absorber masses can be different. In both cases the analysis of the obtained formulas shows that the effective width of the Lorentzian profile increases with speed dependence of collisional shift, and at the same time it is reduced by speed dependence of collisional width. Moreover the effective shift of the Lorentzian profile is modified by thermal average of speed dependence of the product of collisional width and shift. A comparison of the line shape parameters determined from the derived analytical formulae and numerical calculations was carried out in the articles. This comparison showed good agreement between the results obtained analytically and numerically. Given the high computational cost of numerical calculations, the analytical formulae presented in the work [G,H] can provide an alternative when determining the shape of collision-induced spectral lines in the regime of the frequent velocity-changing collisions.

In summary, the presented dissertation is dedicated to the problem of modelling line profiles from first principles. The results presented in this dissertation are relevant not only to a number of studies in the field of ultraprecise spectroscopy but also to research in astrophysics. In my opinion, the presented work meets the legal requirements for doctoral dissertations specified in Article 187 of the Law on Higher Education and Science of 20 July, 2018 (with subsequent amendments). I recommend that Mr Nikodem Stolarczyk be admitted to the next steps in the procedure for awarding the doctoral degree. At the same time, taking into account the significance of the results presented in the thesis, and their very high scientific level, I propose to distinguish this dissertation.

Reasumując, przedstawiona rozprawa stanowi spójny tematycznie zbiór artykułów poświęconych problematyce modelowania profili linii z zasad pierwszych. Wyniki przestawione w tej rozprawie są istotne nie tylko dla szeregu badań z zakresu ultraprecyzyjnej spektroskopii ale i dla badań z zakresu astrofizyki. W mojej opinii przedstawiona praca spełnia ustawowe wymogi stawiane rozprawom doktorskim określone w art. 187 ustawy Prawo o szkolnictwie wyższym i nauce z dnia 20 lipca 2018r. (z późniejszymi zmianami). Wnoszę więc o dopuszczenie mgr. Nikodema Stolarczyka do dalszych czynności przewodu doktorskiego. Jednocześnie, biorąc pod uwagę znaczenie wyników przedstawionych w rozprawie oraz ich bardzo wysoki poziom naukowy, wnioskuję o wyróżnienie tej rozprawy.

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