REVIEW OF THE DISSERTATION ENTITLE “COLLISION-INDUCED LINE-SHAPE EFFECTS IN MOLECULAR SPECTRA” BY NIKODEM STOLARCZYK

Molecular line-shape studies are essential for many applications, such as highly accurate atmospheric greenhouse gas remote sensing, which requires precision better than a few per mill for calculated absorption cross-sections. They are also crucial for planetary research and gas metrology, with increasing needs for extremely accurate characterization of molecular line shapes across broad temperature and pressure ranges. In high-resolution spectroscopy, phenomenological models are widely used to represent spectral line shapes. The parameters of these models, known as line-shape parameters, are typically determined from laboratory measurements. However, this represents a significant experimental effort to fulfill spectroscopic databases and applications that require a large number of lines under broad pressure and temperature ranges for various molecular systems. Moreover, due to the empirical nature of the models used, extrapolations of line-shape parameters for unmeasured conditions of pressure and temperature can be hazardous.

In this context, the present thesis work is devoted to the development and refinement of a methodology for determining accurate spectral line profile parameters using first-principle calculations. First, ab initio calculations are performed to compute accurate potential energy surfaces representing the intermolecular interactions. These are then used in quantum scattering calculations to enable the computation of the generalized spectroscopic collision cross-sections. From these, line-shape parameters and their temperature dependences, compatible with spectroscopic databases, are deduced and provided. At each step of the procedure, the methodology has been successfully tested and validated against highly accurate experimental spectra. Ultimately, expansive datasets of spectral line-shape parameters for the HITRAN database, as well as application-oriented datasets for astrophysical research, have been provided and can be used for various applications as mentioned above.

Eight papers (A-H), published in peer-reviewed international journals with high impact factors, have resulted from this thesis work. Papers A, B, C, E, and F focused on validating the developed theoretical spectral lines by comparing them with highly accurate experimental spectra. Articles C and D aim to provide complete and comprehensive datasets, enabling the simulation of spectral lines of the two isotopologues of molecular hydrogen with minimal effort while maintaining high accuracy. Finally, papers G and H are devoted to a new approach to modeling spectral lines in the regime of frequent velocity-changing collisions.

In paper F, ab initio calculations of the spectral line shape have been directly tested by comparison with experimental data of the 3-0 S(1) and 2-0 Q(1) lines of H_2 perturbed by He. The influence of different collisional effects on the calculated spectra was investigated, showing that both line broadening and shifting, their speed dependences, and the complex Dicke narrowing play important roles in the resulting spectra. The influence of the centrifugal distortion on the ab initio calculated potential energy surface was also investigated. It shows that accounting for this effect leads to changes of up to 6% in the calculated line-shape parameters of the 3-0 S(1) line but has no influence on the 2-0 Q(1) line, due to the large contribution of vibrational dephasing to the line broadening of H_2-He.

The methodology developed was applied to the case of the 3-0 S(1) line of H_2 perturbed by Ar in paper A. This molecular system, presenting a high mass ratio between the collisional partners and pronounced speed dependence of collisional broadening and shift, provides an interesting test of

the method used. The generalized spectroscopic sections were computed by solving the close-coupling equations using the MOLSCAT code. The ab initio calculation-derived speed-dependent line broadening and shifting coefficients were then used together with the billiard-ball profile to simulate absorption spectra under the same conditions as the experiments. The latter were performed with a cavity ring-down spectrometer at four pressures, from 25 kPa to 98 kPa. Simulated spectra are in 2.65% agreement with measured data. Adjusting the pressure shift in the comparison decreased the relative Root Mean Square Error (rRMSE) to 1.58%, but the adjusted value of the pressure shift is 20% larger than the calculated one. Analysis showed that this difference between the theoretically calculated line shift and the measured one is probably due to inaccuracies in the used potential energy surface.

In paper B, the methodology has been validated against experimental data of the R(0) line of CO perturbed by collisions with Ar at pressures from 52.1 mTorr to 1525 Torr, measured with three different spectrometers. The generalized spectroscopic collisional cross-sections were computed using the MOLSCAT code and two potential energy surfaces. Off-diagonal elements of the relaxation matrix were also calculated for intra- and inter-branch line-mixing. Line-shape parameters associated with the van Vleck-Weisskopf profile, including the first-order line mixing and quadratic speed dependence, were determined from the computed generalized spectroscopic cross-sections and off-diagonal relaxation matrix elements. These parameters and profiles were used to simulate spectra under the same conditions as the measurements. Direct comparisons between simulated spectra and experimental data showed very good agreement, with rRMSE within 1% and below 0.5% if line areas were retrieved. These line-shape parameters were also determined for a wide range of temperatures from 10 K to 700 K, enabling the determination of their temperature dependences using the DPL.

In papers C and D, the methodology was applied to rovibrational lines of H_2 and HD perturbed by He. Line-shape parameters and their temperature dependences, compatible with the HITRAN spectroscopic database, were computed for 3480 H2 lines and 11575 HD lines in various rovibrational bands. These data enable modeling the entire rovibrational spectrum of H_2 and HD with high accuracy (below 1% for the lines tested in the papers), at a temperature range between 20 and 1000 K. These data are now available in the HITRAN database.

Paper E is devoted to accurate collision-induced line-shape parameters for three pure rotational lines of HD perturbed by H_2. These lines are currently used for the analysis of the giant planets' atmospheres. A new, highly accurate potential energy surface was computed for this system. The collisional line broadening, shifting, their speed dependences, and the complex Dicke narrowing parameter were calculated for a large temperature range. Theoretically calculated values were validated by comparison with experimental data measured by a cavity ring-down spectrometer. The provided line-shape parameters and their temperature dependences are compatible with the HITRAN database format. The accuracy of the spectral line-shape models at thermodynamic conditions known to be present in the atmospheres of the Solar System's giant planets was analyzed, showing that a key role is played by the speed dependence of collisional broadening and shift, as well as the Dicke effect. Therefore, applying the traditional Voigt profile might alter the effective height and width of the spectral line by as much as a factor of two.

In papers G and H, the behavior of the spectral lines in the regime of frequent velocity-changing collisions has been explored. It has been shown that some sophisticated line profiles, accounting

for both the speed dependence of the line broadening and shifting coefficients and the complex Dicke narrowing effect, are equivalent to a simple Lorentzian profile with effective line width and shift. Analytical formulas for calculating these effective line widths and shifts have been provided. These enabled showing that the speed dependence of collisional width gives rise to effective narrowing of the line, while the presence of the speed dependence of the collisional shift broadens the profile. This work is of great importance since it extends the applicability of the aforementioned methodology to this regime at significantly lower computational cost.
The results obtained in this thesis are of major importance for future line-shape studies and spectroscopic databases and applications. They contribute to understanding the different physical mechanisms that contribute to the spectral shape of optical transitions. These results have been the subject of eight papers published in peer-reviewed international journals, proving the interest in and the quality of the research performed in this thesis.

The submitted doctoral dissertation by Mr. Nikodem Stolarczyk entitled "Collision-induced line-shape effects in molecular spectra" demonstrates the candidate's comprehensive theoretical knowledge in the field of physical sciences and his ability to conduct independent scientific research. This theoretical knowledge is presented on multiple levels. The dissertation offers an original solution to several scientific problems. I assess it positively and recommend that it be allowed for public defense. In view of its outstanding quality, I strongly request that it be considered for an award of distinction.

Paris, July 12, 2024

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Directrice de Recherche au CNRS

LMD/IPSL, CNRS, Sorbonne Université