MOLECULAR LINE-SHAPE MODELING FROM FIRST PRINCIPLES
Piotr Wcislo, Franck Thibault, Hubert Cybulski, Ha Tran, Frédéric Chaussard, Roman Ciurylo

To cite this version:

HAL Id: hal-01263170
https://hal.archives-ouvertes.fr/hal-01263170
Submitted on 21 Feb 2016

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
We performed **ab initio** calculations of the $\text{H}_2$-$\text{Ar}$ collisions and applied them to the simulation of the shape of anomalously broadened $\text{H}_2$ Q(1) line perturbed by Ar [1].

- We performed highly accurate **ab initio** calculations of the three dimensional $\text{H}_2$-$\text{Ar}$ potential energy surface (PES).
- We calculated generalized cross sections for line broadening and shifting by solving the close-coupling (CC) equations.
- We used a hard-sphere approximation of the $\text{H}_2$-$\text{Ar}$ potential to describe velocity-changing collisions.
- We performed highly accurate curves at the mean collision energy.
- The hard-sphere diameters were chosen.

**Why?**

- For the $\text{H}_2$-$\text{Ar}$ systems, fundamental discrepancies were reported [6,8] between experimental broadening coefficients [4,5] and thermally averaged close-coupling pressure broadening cross-sections.
- To understand the role of the velocity-changing collisions in the anomalous inhomogeneity in the $\text{Ar}$-broadening of the H2 Q(1) line.
- The **ab initio** modeling of molecular line shape is essential to eliminate systematic errors in optical metrology based on molecular spectroscopy.

**How?**

- The hard-sphere diameters were chosen such as to obtain the lowest cross sections at the mean collision energy ($\sigma_0 = 4\hbar^2$).
- Frequency of the velocity-changing collisions for a fixed $\text{Ar}$-perturber velocity.
- The first-order approximation is given by.

**VELOCITY-CHANGING COLLISIONS**

- We demonstrated that, to properly describe the velocity-changing collisions, the $\text{H}_2$, $\text{H}_2$, and $\text{H}_2$-$\text{Ar}$ potentials can be approximated by hard-sphere models [9].

**LINE-SHAPE MODEL**

- Speed-dependent billiard-ball profile [12]
- Transport/relaxation equation: stationary version of a Lollwitz equation
- Absorption
- Speed-dependent broadening and shifting
- Maxwellian distribution
- Billiard-ball velocity-changing operator
- We assume that the velocity-changing collisions are not significantly phase/state-changing collisions
- We demonstrated that for the $\text{H}_2$-$\text{Ar}$ system, due to a very strong shift speed dependence, the final line width dramatically depends on the description of the velocity-changing collisions [13].

**PHASE/STATE-CHANGING COLLISIONS**

- For the purpose of CC calculations we projected the PES on $\text{H}_2$ vibrational states and on Legendre polynomials (the angle dependence).
- Generalized spectroscopic cross sections over perturber velocity.

**COMPARISON WITH EXPERIMENTAL DATA**

- Our approach eliminates fundamental discrepancies between simulated and measured broadening for H2 Q(1) line perturbed by Ar [15]. We also compare the shapes of experimental lines with **ab initio** calculations.

**REFERENCES**


Project supported by the Foundation for Polish Science Team Programme co-financed by the EU European Regional Development Fund, Operational Program Innovative Economy.

The research was co-financed by the National Science Centre, Project No. DEC-2013/09/N/ST4/00327 and Foundation for Polish Science START project. The financial support provided by the French-Polish "Program Hubert Curien" POLONIUM program is acknowledged.