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► **To cite this version:**

Piotr Wcislo, Franck Thibault, Hubert Cybulski, Ha Tran, Frédéric Chaussard, et al.. MOLECULAR LINE-SHAPE MODELING FROM FIRST PRINCIPLES. The 24th Colloquium on High Resolution Molecular Spectroscopy HRMS 2015, Aug 2015, Dijon, France. . hal-01263170

**HAL Id: hal-01263170**

**<https://hal.science/hal-01263170>**

Submitted on 21 Feb 2016

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# MOLECULAR LINE-SHAPE MODELING FROM FIRST PRINCIPLES

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## What? →

We performed *ab initio* calculations of H<sub>2</sub>-Ar collisions and applied them to the simulation of the shape of anomalously broadened H<sub>2</sub> Q(1) line perturbed by Ar [1]

- We performed highly accurate *ab initio* calculations of the three dimensional H<sub>2</sub>-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 H<sub>2</sub>-Ar potential to describe velocity-changing collisions.
- We simulated the shape of H<sub>2</sub> line perturbed by Ar by solving the transport/relaxation equation for optical coherences [2,3].

## Why? →

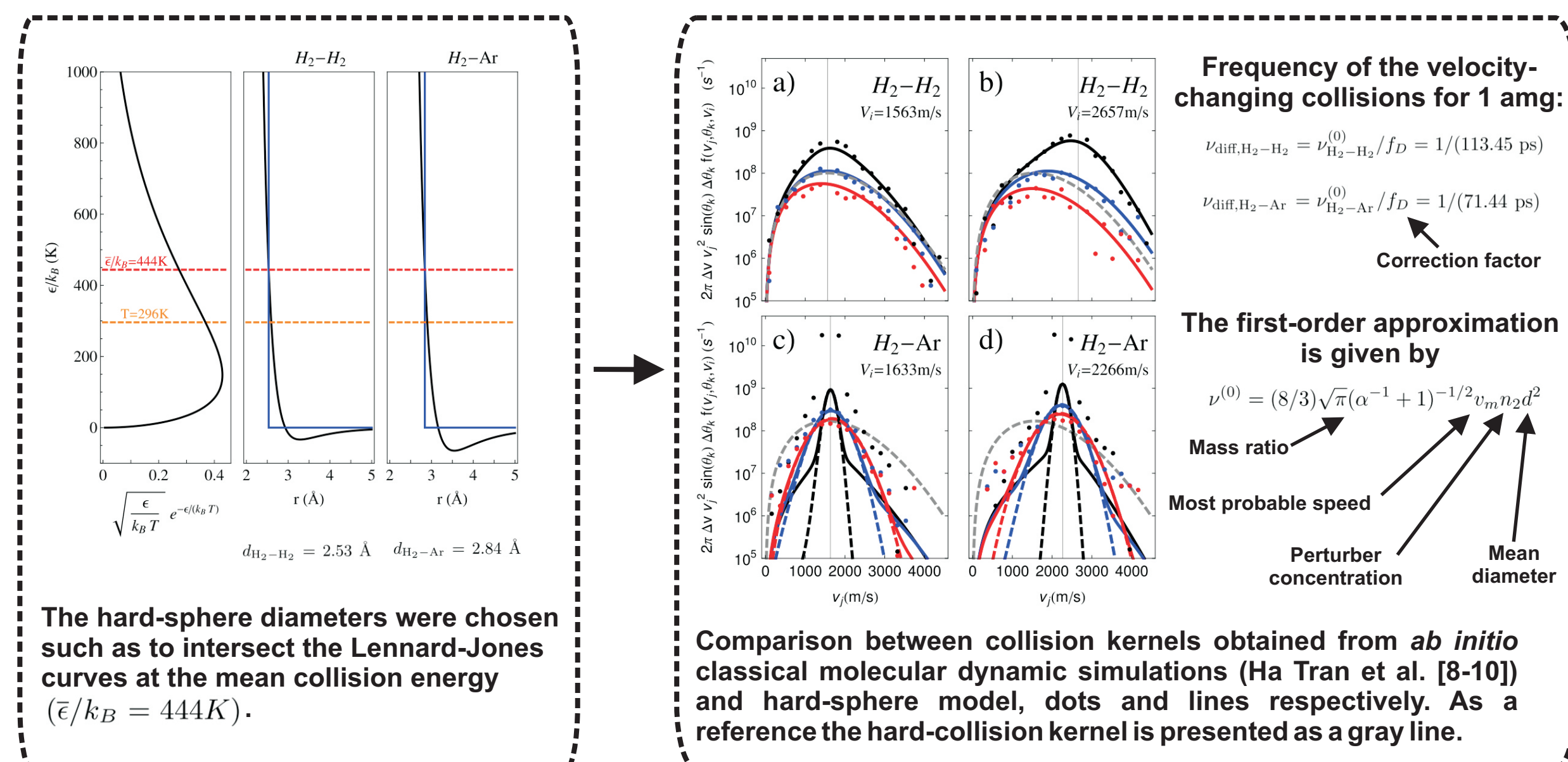
For the H<sub>2</sub>/D<sub>2</sub>-Ar systems, fundamental discrepancies were reported [6,8] between experimental broadening coefficients [4,5] and thermally averaged close-coupling pressure broadening cross-sections

- To understand the role of the velocity-changing collisions in the anomalous inhomogeneity in the Ar-broadening of the H<sub>2</sub> Q(1) line.
- The *ab initio* modeling of molecular line shape is essential to eliminate systematic errors in optical metrology based on molecular spectroscopy.

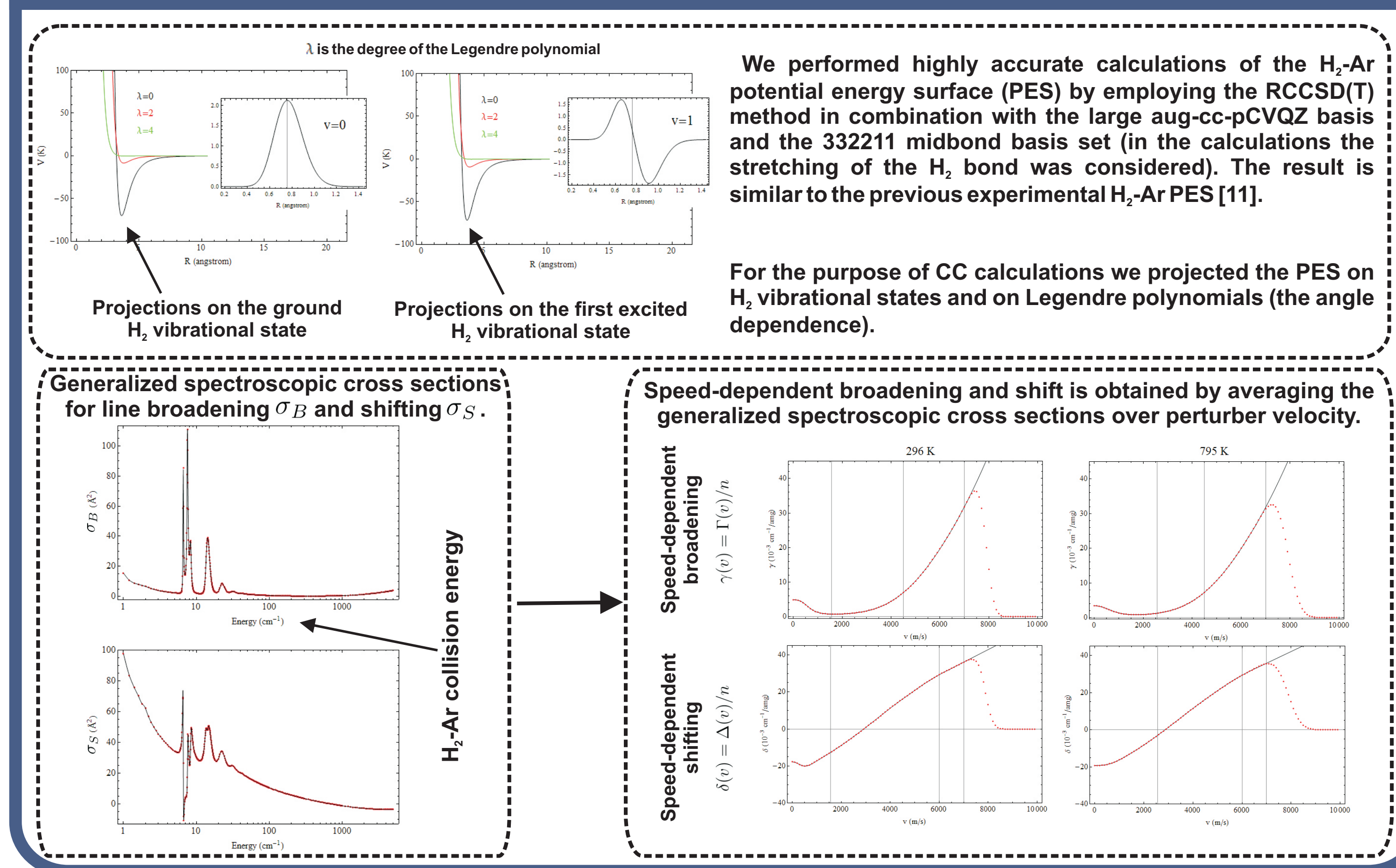
## How? ↓

### VELOCITY-CHANGING COLLISIONS

We demonstrated that, to properly describe the velocity-changing collisions, the H<sub>2</sub>-H<sub>2</sub> and H<sub>2</sub>-Ar potentials can be approximated by hard-sphere models [9].



### PHASE/STATE-CHANGING COLLISIONS



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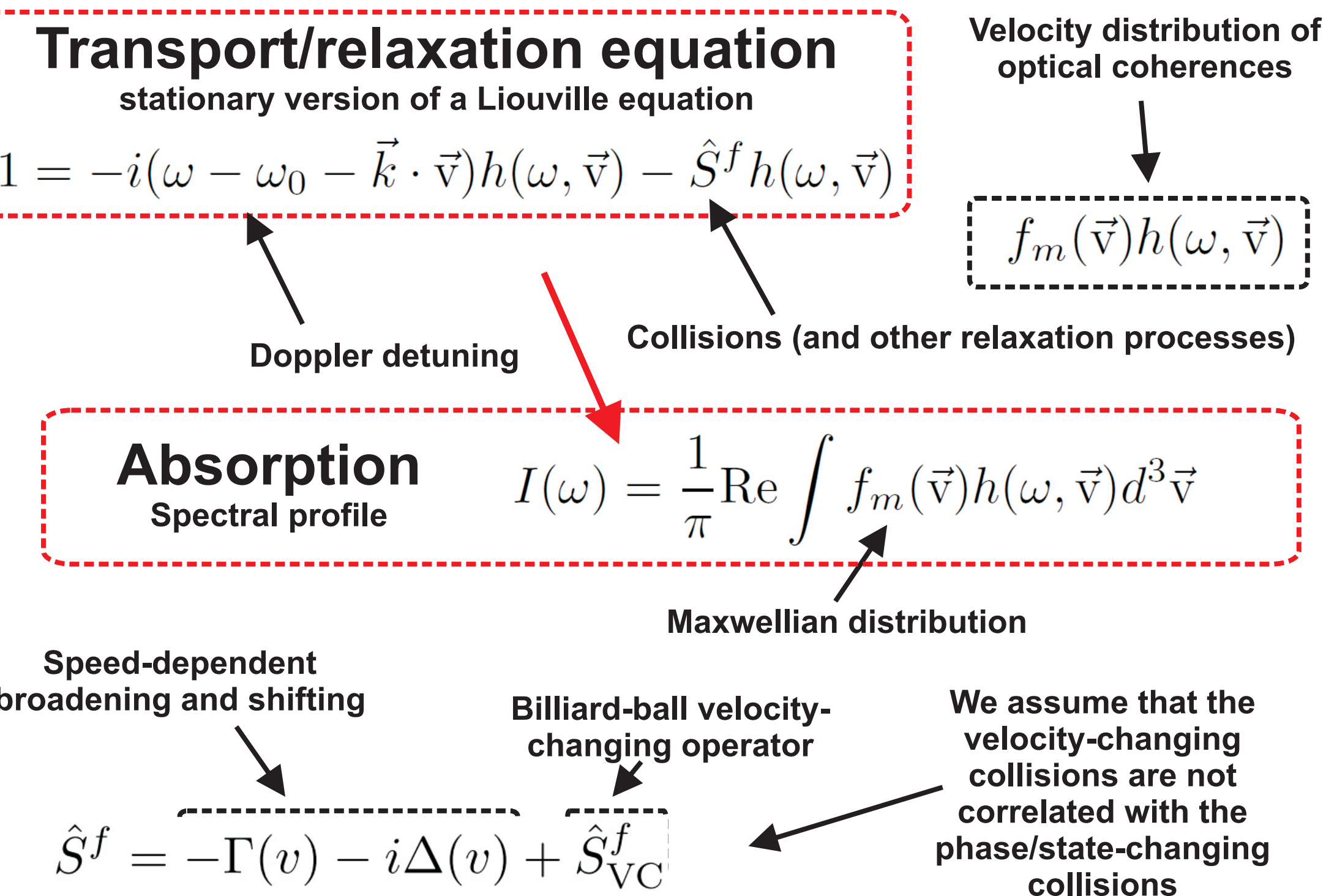
Project supported by the Foundation for Polish Science Team Programme co-financed by the EU European Regional Development Fund, Operational Program Innovative Economy.

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 "Programm Hubert Curien" POLONIUM program is acknowledged.



### LINE-SHAPE MODEL

#### Speed-dependent billiard-ball profile [12]



### COMPARISON WITH EXPERIMENTAL DATA

Our approach eliminates fundamental discrepancies between simulated and measured broadening for H<sub>2</sub> Q(1) line perturbed by Ar [13]. We also compare the shapes of experimental lines with *ab initio* calculations.

