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MOLECULAR LINE-SHAPE MODELING FROM FIRST PRINCIPLES

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What? →

We performed *ab initio* calculations of H₂-Ar collisions and applied them to the simulation of the shape of anomalously broadened H₂ Q(1) line perturbed by Ar [1]

- We performed highly accurate *ab initio* calculations of the three dimensional H₂-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 H₂-Ar potential to describe velocity-changing collisions.
- We simulated the shape of H₂ line perturbed by Ar by solving the transport/relaxation equation for optical coherences [2,3].

Why? →

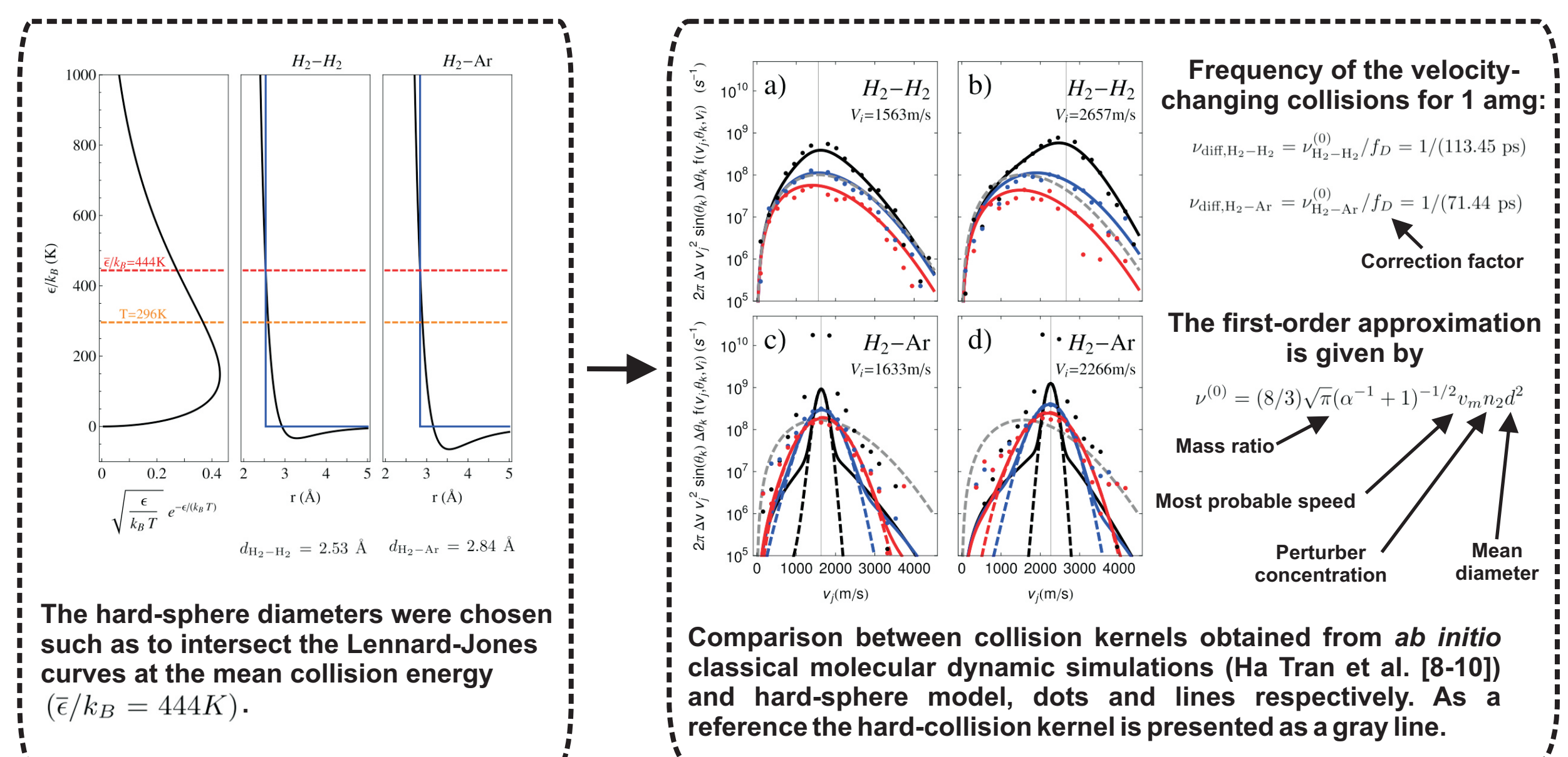
For the H₂/D₂-Ar systems, fundamental discrepancies were reported [6,8] between experimental broadening coefficients [4,5] and thermally averaged close-coupling pressure broadening cross-sections

- To understand the role of the velocity-changing collisions in the anomalous inhomogeneity in the Ar-broadening of the 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.

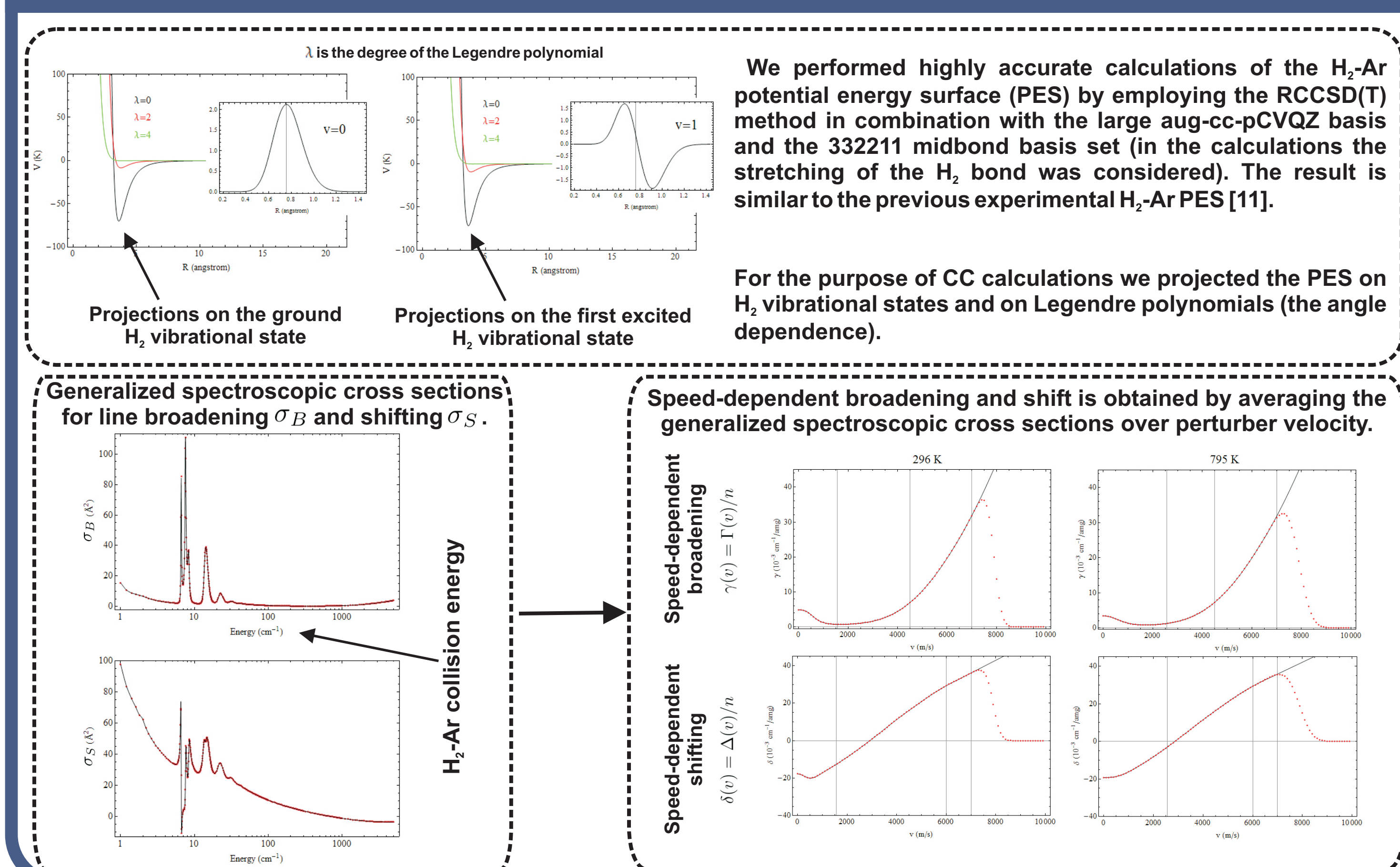
How? ↓

VELOCITY-CHANGING COLLISIONS

We demonstrated that, to properly describe the velocity-changing collisions, the H₂-H₂ and H₂-Ar potentials can be approximated by hard-sphere models [9].



PHASE/STATE-CHANGING COLLISIONS



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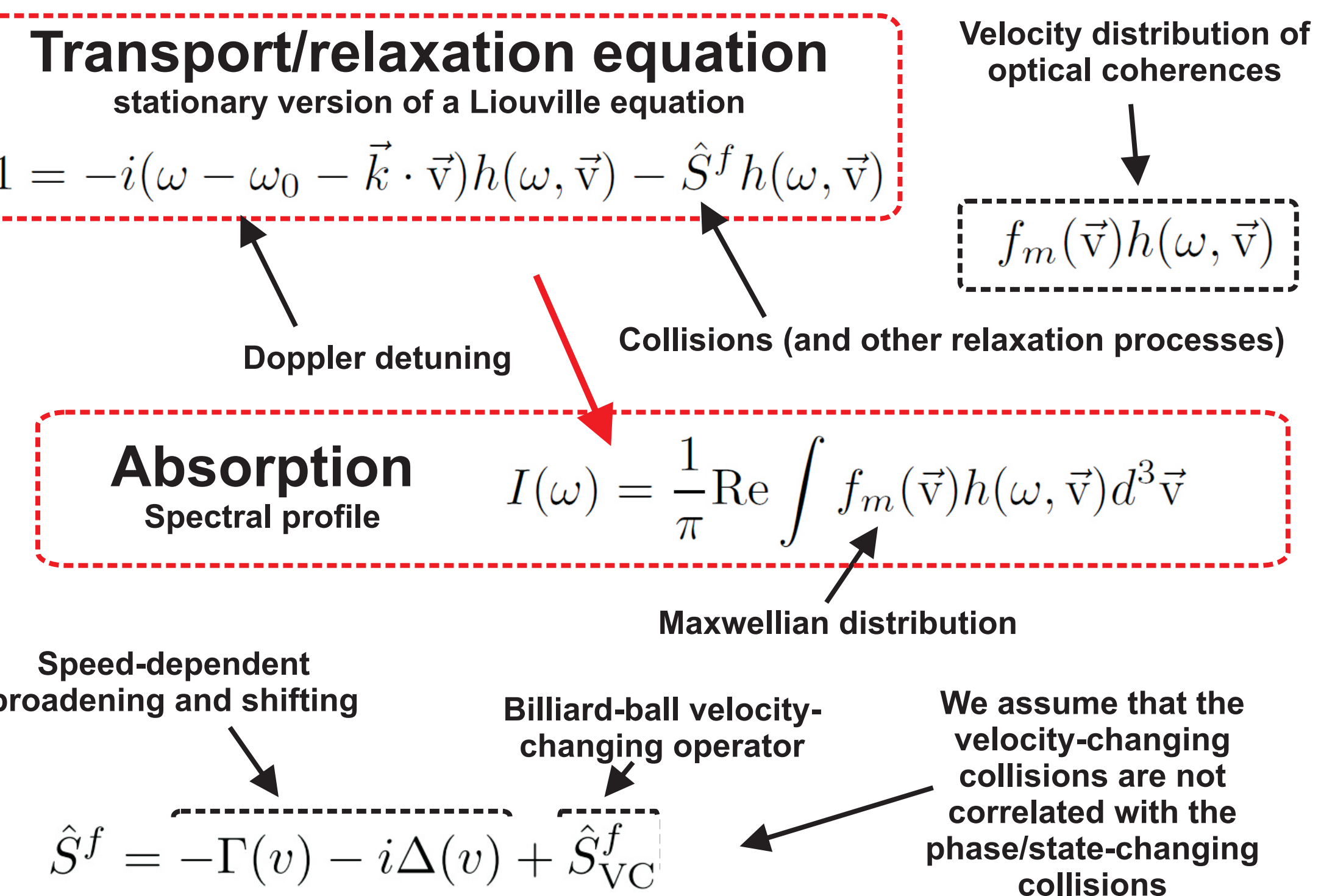
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LINE-SHAPE MODEL

Speed-dependent billiard-ball profile [12]



COMPARISON WITH EXPERIMENTAL DATA

Our approach eliminates fundamental discrepancies between simulated and measured broadening for H₂ Q(1) line perturbed by Ar [13]. We also compare the shapes of experimental lines with *ab initio* calculations.

