MOLECULAR LINE-SHAPE MODELING FROM FIRST PRINCIPLES
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MOLECULAR LINE-SHAPING FROM FIRST PRINCIPLES


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**What?**

- **We performed** *ab initio* calculations of the H-Ar system and applied them to the simulation of the anomalous broadening of H, Q(1) line perturbed by Ar [1].
- **We performed** highly accurate *ab initio* calculations of the three dimensional H-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-Ar potential to describe velocity-changing collisions.
- We simulated the shape of H line perturbed by Ar by solving the transport/relaxation equation for optical coherence [2,3].

**Why?**

- 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.

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**How?**

**VELOCITY-CHANGING COLLISIONS**

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

**PHASE/STATE-CHANGING COLLISIONS**

- The hard-sphere diameters were chosen such as to obtain the Lennard-Jones curves at the mean collision energy (\(E_c = 1000\) K).
- We plotted the generalized spectroscopic cross sections for the broadening and shifting of H, vibrational state.

**LINE-SHAPE MODEL**

- Speed-dependent billiard-ball profile [12]

**COMPARISON WITH EXPERIMENTAL DATA**

- Speed-dependent Doppler broadening and shifting

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**REFERENCES**


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