Strong competition between velocity-changing and phase/state changing collisions in H_2 spectra perturbed by Ar

P. Wcisło[1], F. Thibault[2], H. Cybulski[1], and R. Ciuryło[1]

[1] *Institute of Physics, Astronomy and Informatics, Nicolaus Copernicus University, Grudziadzka 5/7, 87-100 Toruń, Poland*
[2] *Institut de Physique de Rennes, UMR CNRS 6251, Université de Rennes 1, Campus de Beaulieu, Bât.11B, F-35042 Rennes, France*

Presenting Author: piotr.wcislo@fizyka.umk.pl

For the H_2/D_2-Ar systems, fundamental discrepancies between thermally averaged collisional broadening obtained from experimentally determined law [1,2] and from *ab initio* close-coupling (CC) calculations were reported [3-5]. For instance at room temperature the broadening of the Q(1) line calculated from the experimental law was almost two times larger than the theoretical one.

To resolve the problem of these huge discrepancies we performed highly accurate calculations of the H_2-Ar potential energy surface (PES) by employing the RCCSD(T) method in combination with the large aug-cc-pCVQZ basis and the 332211 midbond basis set (in the calculations the stretching of the H_2 bond was considered). However, we found that the broadening of the H_2 Q(1) line determined from the CC calculations based on the new PES is even less consistent with the value from experimental law than the previous CC calculations based on less accurate, earlier PES [6]. Next, we modified the line-shape model replacing the phenomenological model of the velocity-changing collisions by much more physical *ab initio* billiard-ball model, for which it was already shown that it provides appropriate description of the velocity-changing collisions for the H_2-Ar system [7]. We found that this approach gives the H_2 Q(1) line broadening, for the mixture of 5% of H_2 and 95% of Ar, very close to experimental values, see Fig. 1. Our model not only properly handles the dynamics of optically active molecules (in particular a strong competition between velocity-changing and phase/state-changing collisions), but also constitutes a first step toward application of advanced *ab initio* line-shape models in ultra-accurate optical metrology based on molecular spectroscopy.

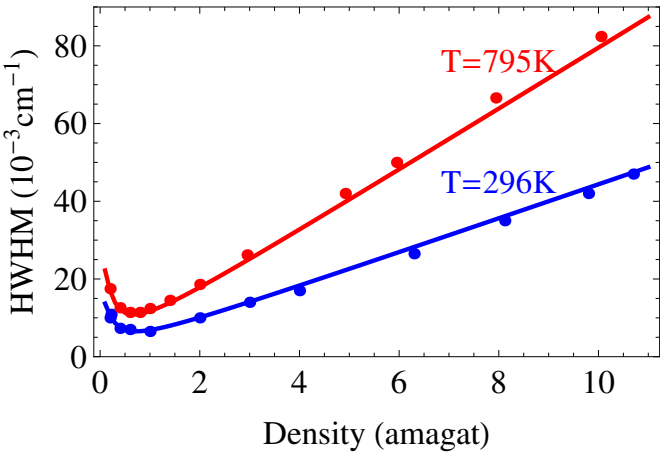

Figure 1: *HWHM of the H_2 Q(1) line as a function of density for mixture of 5% H_2 and 95% Ar. Dots represent experimental results [2], while the lines correspond to our ab initio calculations.*

References

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