MOLECULAR LINE-SHAPE MODELING FROM FIRST PRINCIPLES

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What?

We performed *ab initio* calculations of H_2-Ar collisions and applied them to the simulation of the shape of anomalously broadened H_2 Q(1) line perturbed by Ar [1]

- We performed highly accurate *ab initio* calculations of the three dimensional H_2-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_2-Ar potential to describe velocity-changing collisions.
- We simulated the shape of H_2 line perturbed by Ar by solving the transport/relaxation equation for optical coherences [2,3].

Why?

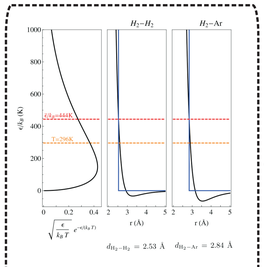
For the H_2/D_2-Ar systems, fundamental discrepancies were reported [6,8] between experimental broadening coefficients [4,5] and thermally averaged close-coupling pressure broadening cross-sections

- 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.

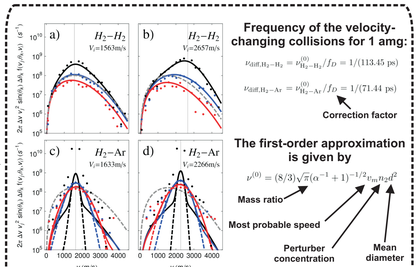
How?

VELOCITY-CHANGING COLLISIONS

We demonstrated that, to properly describe the velocity-changing collisions, the H_2-H_2 and H_2-Ar potentials can be approximated by hard-sphere models [9].



The hard-sphere diameters were chosen such as to intersect the Lennard-Jones curves at the mean collision energy $(\bar{\epsilon}/k_B = 444K)$.



Frequency of the velocity-changing collisions for 1 amg:

$\nu_{\mathrm{diff},H_2-H_2} = \nu^{(0)}_{H_2-H_2}/f_D = 1/(113.45\ \mathrm{ps})$

$\nu_{\mathrm{diff},H_2-Ar} = \nu^{(0)}_{H_2-Ar}/f_D = 1/(71.44\ \mathrm{ps})$

Correction factor

The first-order approximation is given by

$\nu^{(0)} = (8/3)\sqrt{\pi}(\alpha^{-1}+1)^{-1/2}v_m n_{2d} d^2$

Mass ratio

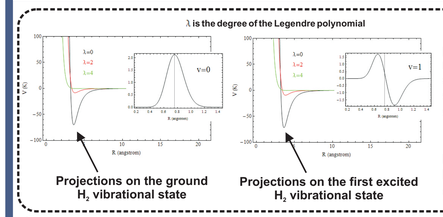
Most probable speed

Perturber concentration

Mean diameter

Comparison between collision kernels obtained from *ab initio* classical molecular dynamic simulations (Ha Tran et al. [8-10]) and hard-sphere model, dots and lines respectively. As a reference the hard-collision kernel is presented as a gray line.

PHASE/STATE-CHANGING COLLISIONS



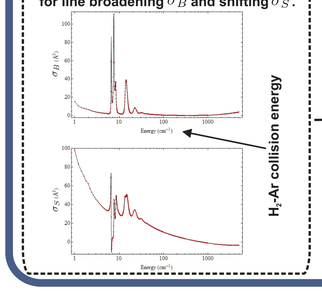
Projections on the ground H_2 vibrational state

Projections on the first excited H_2 vibrational state

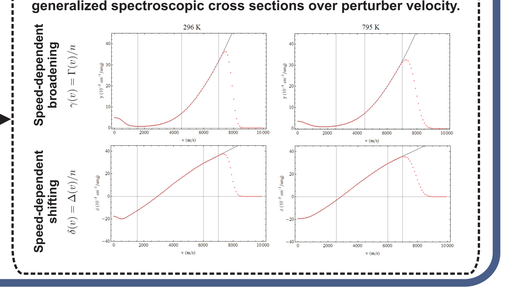
We performed highly accurate calculations of the H_2-Ar potential energy surface (PES) by employing the RCCSD(T) method in combination with the large aug-cc-pCVQZ basis and the 332211 midbond basis set (in the calculations the stretching of the H_2 bond was considered). The result is similar to the previous experimental H_2-Ar PES [11].

For the purpose of CC calculations we projected the PES on H_2 vibrational states and on Legendre polynomials (the angle dependence).

Generalized spectroscopic cross sections for line broadening σ_B and shifting σ_S.



Speed-dependent broadening and shift is obtained by averaging the generalized spectroscopic cross sections over perturber velocity.



LINE-SHAPE MODEL

Speed-dependent billiard-ball profile [12]

Transport/relaxation equation
stationary version of a Liouville equation

$$1 = -i(\omega - \omega_0 - \vec{k}\cdot\vec{v})h(\omega,\vec{v}) - \hat{S}^f h(\omega,\vec{v})$$

Velocity distribution of optical coherences

$$f_m(\vec{v})h(\omega,\vec{v})$$

Doppler detuning

Collisions (and other relaxation processes)

Absorption
Spectral profile

$$I(\omega) = \frac{1}{\pi}\mathrm{Re}\int f_m(\vec{v})h(\omega,\vec{v})d^3\vec{v}$$

Maxwellian distribution

Speed-dependent broadening and shifting

Billiard-ball velocity-changing operator

We assume that the velocity-changing collisions are not correlated with the phase/state-changing collisions

$$\hat{S}^f = -\Gamma(v) - i\Delta(v) + \hat{S}^f_{\mathrm{VC}}$$

COMPARISON WITH EXPERIMENTAL DATA

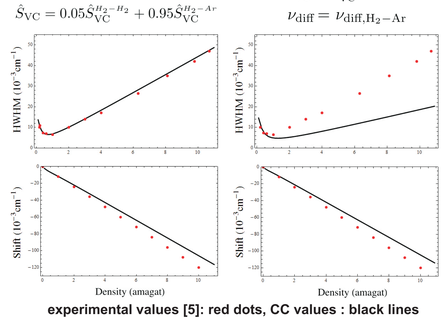
Our approach eliminates fundamental discrepancies between simulated and measured broadening for H_2 Q(1) line perturbed by Ar [13]. We also compare the shapes of experimental lines with *ab initio* calculations.

We demonstrated that for the H_2-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]

$\hat{S}_{\mathrm{VC}} = 0.05\hat{S}^{H_2-H_2}_{\mathrm{VC}} + 0.95\hat{S}^{H_2-Ar}_{\mathrm{VC}}$

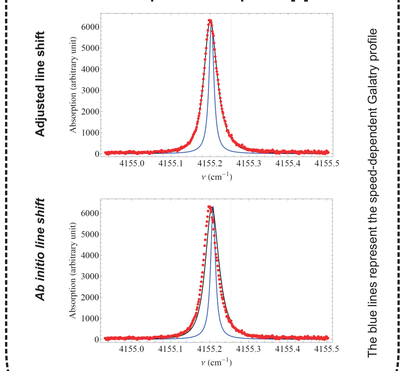
$\hat{S}_{\mathrm{VC}} = \hat{S}^{H_2-H_2}_{\mathrm{VC}}$

$\nu_{\mathrm{diff}} = \nu_{\mathrm{diff},H_2-Ar}$



experimental values [5]: red dots, CC values : black lines

Comparison of *ab initio* line shape with experimental spectra [5]



The blue lines represent the speed-dependent Galatry profile

REFERENCES

[1] Farrow R L, Rahn L A, Sitz G O, Rosasco G O 1989 Phys. Rev. Lett. 63, 746-49

[2] Blackmore R 1987 J. Chem. Phys. 87, 791-800

[3] May A D, Liu W-K, McCourt FRW, et al. 2013 Can. J. Phys. 91, 879-895

[4] Berger J , Saint-Loup R, Berger H, et al. 1994 Phys. Rev. A 49, 3396-406

[5] Chaussard F, Michaut X, Saint-Loup R, et al. 2000 J. Chem. Phys. 112, 158-66

[6] Waldron L, Liu W-K 2001 J. Chin. Chem. Soc. 48, 439-48

[7] Waldron L, Liu W-K, Le Roy R J 2002 J. Mol. Struct. 591, 245-53

[8] Tran H, Thibault F, Hartmann J-M 2011 J. Quant. Spectrosc. Radiat. Transfer 112, 1035

[9] Wcisło P, Tran H, Kassi S, et al. 2014 J. Chem. Phys. 141, 074301

[10] Tran H, Hartmann J-M, Chaussard F, Gupta M 2009 J. Chem. Phys. 131, 154303

[11] Bissonnette C, Chuaqui CE, Crowell KG, et al. 1996 J. Chem. Phys. 105, 2639-53

[12] Ciuryło R, Shapiro D A, Drummond J R, May A D 2002 Phys. Rev. A 65, 012502-8

[13] Wcisło P, Thibault F, Cybulski H, Ciuryło R 2015 Phys. Rev. A 91, 052505

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