

### 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 $H_2$ Q(1) line perturbed by Ar [1]

- $\rightarrow$  We performed highly accurate *ab initio* calculations of the three dimensional H<sub>2</sub>-Ar potential energy surface (PES).
- $\rightarrow$  We used a hard-sphere approximation of the H<sub>2</sub>-Ar potential to describe velocity-changing collisions.

## How?



### **MOLECULAR LINE-SHAPE MODELING FROM FIRST PRINCIPLES** <sup>1</sup>Piotr Wcisło, <sup>2</sup>Franck Thibault, <sup>1</sup>Hubert Cybulski, <sup>3</sup>Ha Tran, <sup>4</sup>Frédéric Chaussard, <sup>1</sup>Roman Ciuryło <sup>1</sup>Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University, Grudziądzka 5, 87-100 Toruń, Poland <sup>2</sup>Institut de Physique de Rennes, UMR CNRS 6251, Université de Rennes 1, Campus de Beaulieu, Bât.11B, F-35042 Rennes, France <sup>3</sup>Laboratoire Inter-universitaire des Systémes Atmosphériques (LISA), CNRS UMR 7583, Université Paris Diderot, Institut Pierre-Simon Laplace, 94010 Créteil Cedex, France <sup>4</sup>Laboratoire Interdisciplinaire Carnot de Bourgogne (ICB) CNRS (UMR 6303), Université de Bourgogne, BP 47870, F-21078 Dijon Cedex, France For the H<sub>2</sub>/D<sub>2</sub>-Ar systems, fundamental discrepancies Why? 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 → We calculated generalized cross sections for line broadening and shifting by solving the close-coupling (CC) equations. the Ar-broadening of the H2 Q(1) line. → The *ab initio* modeling of molecular line shape is essential to eliminate systematic errors in $\rightarrow$ We simulated the shape of H<sub>2</sub> line perturbed by Ar by solving the transport/relaxation equation for optical coherences [2,3]. optical metrology based on molecular spectroscopy. REFERENCES PHASE/STATE-CHANGING COLLISIONS [1] Farrow R L, Rahn L A, Sitz G O, Rosasco G O 1989 Phys. Rev. Lett. 63, 746-49 We performed highly accurate calculations of the H<sub>2</sub>-Ar potential energy surface (PES) by employing the RCCSD(T) method in combination with the large aug-cc-pCVQZ basis [2] Blackmore R 1987 J. Chem. Phys. 87, 791-800 and the 332211 midbond basis set (in the calculations the stretching of the H<sub>2</sub> bond was considered). The result is [3] May A D, Liu W-K, McCourt FRW, et al. 2013 Can. J. Phys. 91, similar to the previous experimental $H_3$ -Ar PES [11]. 879-895 For the purpose of CC calculations we projected the PES on [4] Berger J, Saint-Loup R, Berger H, et al. 1994 Phys. Rev. A 49, H<sub>2</sub> vibrational states and on Legendre polynomials (the angle 3396-406 [5] Chaussard F, Michaut X, Saint-Loup R, et al. 2000 J. Chem. Speed-dependent broadening and shift is obtained by averaging the generalized spectroscopic cross sections over perturber velocity. 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-[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. COMPARISON WITH EXPERIMENTAL DATA Phys. 105, 2639-53 [12] Ciuryło R, Shapiro D A, Drummond J R, May A D 2002 Phys. Our approach eliminates fundamental discrepancies between simulated and measured broadening for H<sub>2</sub> Rev. A 65, 012502-8 Q(1) line perturbed by Ar [13]. We also compare the shapes of experimental lines with ab initio calculations. [13] Wcisło P, Thibault F, Cybulski H, Ciuryło R 2015 Phys. Rev. A Comparison of *ab initio* line shape 91, 052505 with experimental spectra [5] Project supported by the Foundation for Polish Science Team Programme co-financed by the EU European Regional Development Fund, Operational Program Innovative Economy. 4155.0 4155.1 4155.2 4155.3 4155.4 4155.5 The research was co-financed by the National Science Centre, $\nu (\mathrm{cm}^{-1})$ 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. Foundation for Polich S-1 EUROPEAN UNION EUROPEAN REGIONAL DEVELOPMENT FUND INNOVATIVE ECONOMY 4155.0 4155.1 4155.2 4155.3 4155.4 4155.5









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