Ultra accurate measurements and ab initio calculations of collisional effects in pure D2 .

Mikolaj Zaborowski, Piotr Wcislo, Franck Thibault, Szymon Wójtewicz, Agata Cygan, Grzegorz Kowzan, Piotr Maslowski, Daniel Lisak, Roman Ciurylo

Ultra accurate measurements and *ab initio* calculations of collisional effects in pure D_2.

Ultra accurate measurements and *ab initio* calculations of collisional effects in pure D_2.

Mikołaj Zaborowski*[1], Piotr Wcisło[1], Franck Thibault[2], Szymon Wójtewicz[1], Agata Cygan[1], Grzegorz Kowzan[1], Piotr Masłowski[1], Daniel Lisak[1] and Roman Ciuryło[1]

[1] Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University, Grudziadzka 5, 87-100 Torun, Poland

[2] Institut de Physique de Rennes, UMR CNRS 6251, Université de Rennes 1, Campus de Beaulieu, Bât.11B, F-35042 Rennes, France

E-mail: *`zaborowski@fizyka.umk.pl`

Abstract. We present our experimental spectra of the very weak S(2) transition from the 2–0 band of molecular deuterium, measured with a frequency-stabilized cavity ring-down spectroscopy (FS–CRDS) assisted by the optical frequency comb (OFC). Experimental collisional broadening and shifting are compared with results of *ab initio* quantum scattering calculations.

1. Introduction

With recent developments in the theoretical calculations of molecular state energies of H_2 and its isotopologues [1,2] the transition frequencies with uncertainties exceeding the level of 10^{-3} cm^{-1} for the first overtone band 2-0 became available [3]. Such predictions provide an opportunity to test relativistic and quantum electrodynamics corrections. At this level of accuracy, the line-shape effects, including asymmetry, affect the uncertainty of the determination of H_2, HD and D_2 line positions in the Doppler limit [4].

We have measured the self-broadened spectral line shapes of the very weak S(2) transition of deuterium in the 2–0 band up to the pressure of about 1500 Torr. The collisional effects on the spectral line shape are described using an advanced *ab initio* model. The line has been measured using the well established frequency-stabilized cavity ring-down spectroscopy (FS–CRDS) with the optical frequency axis provided by an optical frequency comb (OFC) [5,6]. Results from the experiment are compared with our *ab initio* quantum scattering calculations of the collisional broadening and shifting coefficients.

2. Experimental setup

The frequency-stabilized cavity ring-down spectrometer used in the experiment has been previously described in [7,8,9]. Here we only provide the details of the recently developed thermal stabilization of the cavity, see Fig. 1.

In our thermal stabilization system four QC–127–1.4–8.5MD *Quick-Cool* Peltier elements, mounted in the top of an insulating box, were used to provide most of the heating or cooling of the optical cavity. ICK PGA 21 x 21 *Fischer Elektronik* heatsinks as well as EB40201S2-000U-999 *SUNON* fans are mounted on both sides of the Peltier devices. Thermoelectric modules are current-driven by a PI controller with an accuracy of 0.01 mA . Depending on the temperature of the cavity, a significant gradient is observed along the cavity. Therefore, three sets of *Minco* thermofoil, silicone-based heaters are attached to different parts of the cavity. Another PI controller (working independently of the main one) is used to make fine local changes of temperature and eliminates the temperature gradient in the cavity.

Three TCS610 *Wavelength Electronics* temperature sensors powered via a 4-wire circuit are

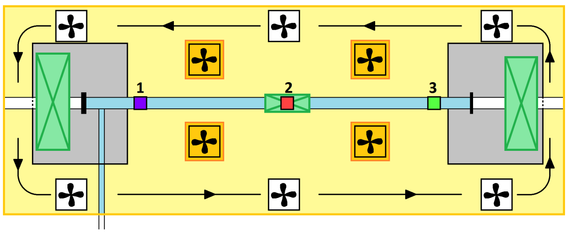

Figure 1. Thermal stabilization of the cavity. Four Peltier cooling/heating modules (orange squares on the top center part above the cavity) effect the major changes of the temperature. For the fine corrections three heaters are directly attached to the cavity (green rectangles). All heaters are thermally isolated from the air next to the cavity and from the thermistors. This way it is possible to reduce temperature differences at the points 1 (violet), 2 (red) and 3 (green) where thermistors are placed.

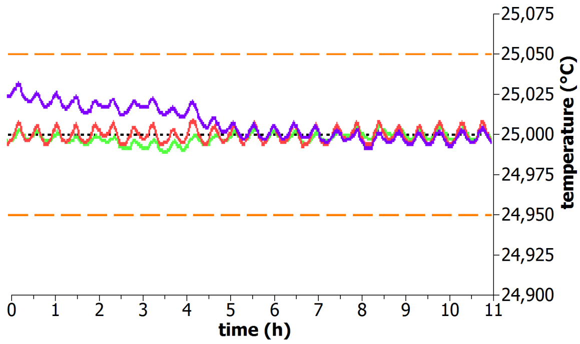

Figure 2. Temperature graph for the stabilization at the temperature of 25°C at the points 1 (violet), 2 (red) and 3 (green) near the cavity, see Fig. 1. With small gradient at the beginning, all temperatures stabilize to the required values in several hours. Orange lines show the deviation from the setting point by 50 mK, which corresponds to the accuracy of the measurement.

arranged at the two sides and at the center of the cavity. They are calibrated with a *Fluke* 5640 Series thermistor at an accuracy of 10 mK at room temperature and 50 mK in the full range from 15°C to 60°C. The heating or cooling is sped up by six EB40201S2-000U-999 *SUNON* fans mounted around the cavity, which also reduce temperature gradient of the gas in the optical cavity. In addition, an electronic system was built to automatically shut down the power supply for the Peltier modules when any heatsink temperature is higher than a set point.

The absolute frequency of the cw-ECDL laser is determined by measuring the heterodyne beat of the CW laser and an optical frequency comb. Both the OFC and the RF signal driving the AOM are referenced to the UTC(AOS) primary frequency standard, provided by the OPTIME network [10,11] from AstroGeodynamic Observatory in Borowiec (Poland) [12,13].

3. Preliminary results and discussion

The spectra were recorded in several pressures between 380 Torr and 1483 Torr and at a temperature of 15.2°C. The average spectrum over 5 scans for the highest pressure is shown in Fig. 3. The measured spectral line shapes were fitted with the Nelkin-Ghatak profile (NGP) [14] which, beyond the Voigt profile approximation, takes into account also the velocity-changing collisions leading to Dicke narrowing. The significant improvement in the quality of the fit (QF) [15], as compared to the VP fit, confirms a large contribution of Dicke narrowing to the line shape. However, the asymmetry of the line is clearly visible. It is a manifestation of the speed-dependence of the collisional shift. This can be confirmed by the flat residuals when the speed-dependent Nelkin-Ghatak profile (SDNGP) [16] is fitted (see Fig. 3). We used the NGP for the estimation of experimental values for pressure broadening and shifting coefficients as well as unperturbed frequency of investigated transition.

The *ab initio* approach was used to compare experimental pressure broadening and shifting coefficients with theoretical ones. We calculated the scattering S-matrix by solving the close-coupling equations for the quantum scattering problem. From the S-matrix we determined the real and imaginary parts of the generalized spectroscopic cross sections, which provide the collisional broadening γ_L/p and shifting δ/p, respectively. The quantum scattering calculations were performed on potential energy surfaces (PES) given by Hinde [17]. The frequency of velocity-changing collisions ν_{VC} is calculated from the diffusion coefficient taken from Ref. [18].

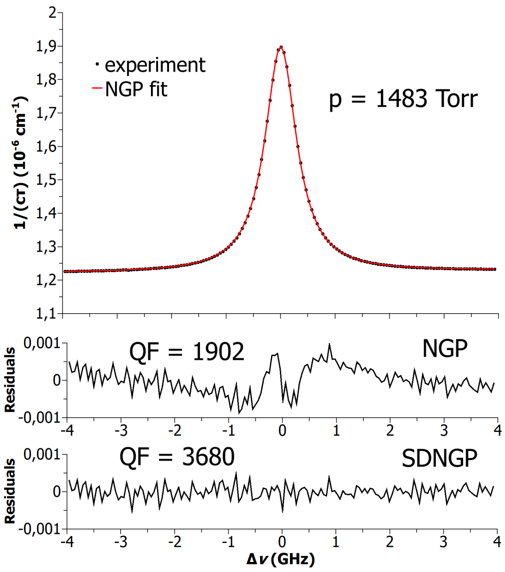

Figure 3. Experimental spectrum of the S(2) 2–0 line of D_2 averaged over 5 scans, recorded with the FS–CRDS technique. Below residuals of the NGP fit (with QF=1902) and the SDNGP fit (with QF=3680).

The theoretical values were compared with the experimental ones obtained from the analysis with the NGP, see Table 1. The values calculated this way show only 6.3% disagreement between the collisional widths but 33% disagreement in collisional shift. This discrepancy in shift, caused by fitting an oversimplified profile neglecting speed-dependent effects, could be explained by non-linear dependence of the collisional shift on pressure [4]. A similar explanation can be given for the large relative difference between the experimentally determined frequency of the velocity-changing collisions ν_{VC} and the calculated one [18].

Finally, we estimated the unperturbed frequency of the S(2) transition from D_2 2–0 band to be equal to 187104.2909(5) GHz. Adding a correction value of 13.2 MHz resulting from the non-linear dependence of the collisional shift on pressure, estimated for a different transition in H_2 [4], to our transition frequency leads to a reasonable agreement with the results of both Mondelain *et al.* [3] — 187104.29951(50) GHz, and Komasa *et al.* [19] — 187104.301(3) GHz.

It is clear that the line-shape model applied in this preliminary characterisation is insufficient. Therefore, a more physical model must be used to correctly describe the recorded spectra. The velocity-changing collisions could be described, for instance, by the hard-sphere approximation of the *ab initio* potential [20,21]. This will be important for further work on verification of quantum electrodynamics in molecular systems [19] as well as for searching for new physics beyond the Standard Model [22].

Table 1. Comparison between our theoretical and experimental (form the NGP fit) values of the collisional width γ_L/p, collisional shift δ/p and frequency of the velocity-changing collisions ν_{VC}.

	γ_L/p (10^{-3} cm^{-1}/amg) (FWHM)	δ/p (10^{-3} cm^{-1}/amg)	ν_{VC}(GHz) for 1483 Torr
calculated	7.21 (this work)	-1.58 (this work)	1.01 (Song [17])
measured (this work)	7.69(5)†	-2.232(7)‡	1.52(2)†

† Obtained from the spectra recorded at 1483 Torr and at 15.2°C.
‡ Obtained from the linear fit performed with the spectra recorded in four pressures (380 Torr, 703 Torr, 1119 Torr and 1483 Torr) at 15.2°C.

Acknowledgments
The project is supported by the National Science Centre, Poland, Projects Nos. 2015/19/D/ST2/02195, DEC-2013/11/D/ST2/02663, 2015/17/B/ST2/02115 and DEC-2012/05/D/ST2/01914. The research is part of the program of the National Laboratory FAMO in Torun, Poland. It is also supported by the COST Action CM1405 MOLIM. The financial support provided by the French-Polish "Programm Hubert Curien" POLONIUM program is acknowledged. P. M. and G. K. are supported by the Foundation for Polish Science HOMING PLUS project.

References

[1] Pachucki K and Komasa J 2010 *Phys. Chem. Chem. Phys.* **12** 9188
[2] Pachucki K and Komasa J 2015 *J. Chem. Phys.* **143** 034111
[3] Mondelain D, Kassi S, Sala T, Romanini D, Gatti D and Campargue A 2016 *J. Mol. Spectrosc.* **326** 5–8
[4] Wcisło P, Gordon I E, Cheng C-F, Hu S-M and Ciuryło R 2016 *Phys. Rev.* A **93** 022501
[5] Domysławska J, Wójtewicz S, Lisak D, Cygan A, Ozimek F, Stec K, Radzewicz C, Trawiński R S and Ciuryło R 2012 *J. Chem. Phys.* **136** 024201
[6] Long D A, Cygan A, van Zee R D, Okumura M, Miller CE, Lisak D and Hodges J T 2012 *Chem. Phys. Lett.* **536** 1–8
[7] Cygan A *et al.* 2015 *Opt. Express* **23** 14472
[8] Cygan A, Wójtewicz S, Zaborowski M, Wcisło P, Guo R, Ciuryło R and Lisak D 2016 *Meas. Sci. Technol.* **27** 045501
[9] Cygan A *et al.* 2016 *J. Chem. Phys.* **144** 214202–1–11
[10] Śliwczyński L *et al.* 2013 *Metrologia* **50** 133
[11] Morzyński P *et al.* 2015 *Sci. Rep.* **5** 17495
[12] Azoubib J *et al.* 2003 *Metrologia* **40** S245
[13] Jiang J *et al.* 2015 *Metrologia* **52** 384
[14] Nelkin M and Ghatak A 1964 *Phys. Rev.* **135** A4
[15] Wcisło P, Cygan A, Lisak D and Ciuryło R 2013 *Phys. Rev. A* **88** 012517
[16] Lance B, Blanquet G, Walrand J and Bouanich J-P 1997 *J. Mol. Spectrosc.* **185** 262–71
[17] Hinde R 2008 *J. Chem. Phys.* **128** 154308
[18] Song B, Wang X and Liu Z 2013 *Mol. Phys.* **111** 49–59
[19] Komasa J, Piszczatowski K, Łach G, Przybytek M, Jeziorski B and Pachucki K 2011 *J. Chem. Theory Comput.* **7** (10) 3105-15
[20] Ciuryło R, Shapiro D A, Drummond J R and May A D 2002 *Phys. Rev. A* **65** 012502
[21] Wcisło P, Tran H, Kassi S, Campargue A, Thibault F and Ciuryło R 2014 *J. Chem. Phys.* **141** 074301
[22] Salumbides E J, Koelemeij J C J, Komasa J, Pachucki K, Eikema K S E and Ubachs W 2013 *Phys. Rev. D* **87** 112008