First-principles calculations of pressure broadening for the case of N 2 -perturbed 118 GHz fine-structure line in O 2 (X 3 Σ –g)

Maciej Gancewski, Hubert Jóźwiak, E. Quintas-Sánchez, R. Dawes, Franck Thibault, P Wcislo

First-principles calculations of pressure broadening for the case of N_2-perturbed 118 GHz fine-structure line in $O_2(X^3\Sigma^-_g)$

M. Gancewski[1], H. Jóźwiak[1], E. Quintas-Sánchez[2], R. Dawes[2], F. Thibault[3], P. Wcisło[1]

1. Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University in Toruń, ul. Grudziądzka 5, 87-100 Toruń, Poland
2. Department of Chemistry, Missouri University of Science and Technology, Rolla, Missouri 65409-0010, USA
3. Univ. Rennes, CNRS, IPR (Institut de Physique de Rennes)-UMR 6251, Rennes F-35000, France

What is this about?

• The general problem: *How is the absorption (emission) spectrum of O_2 modified when it is immersed in the large bath of N_2 molecules?*

• This model question is important in general considerations of atmospheric physics (~78% of N_2 & ~21% of O_2 in our atmosphere…)

• We want to attack this problem *ab initio* style, using methods of theoretical physics and quantum chemistry

• Many spectral lines & bands of O_2 will be affected by its interactions with N_2 in a complicated manner

• A torough study of these is very challenging (preparation of the potential, solving the Schrödinger & kinetic equations...)

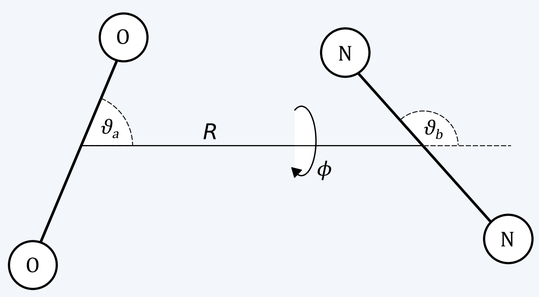
• We thus begin this program by adressing a *simpler* problem: *How much a single isolated line of O_2 is broadened by collisions with N_2 at different gas temperatures?*

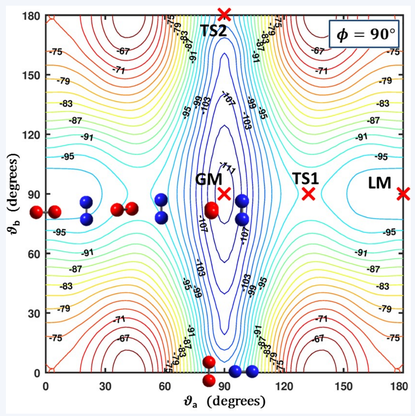
• Here, we consider both (rigid) molecules to be in their ground states & we focus on the N_2-induced perturbations of the isolated *fine-structure* line (centered at ~118 GHz) of $O_2(^3\Sigma)$

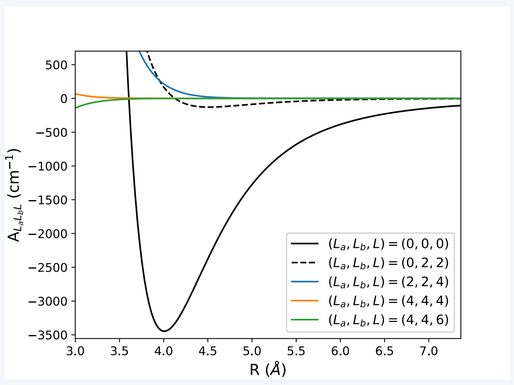
Our methodology

• In $O_2(X^3\Sigma)$ each rotational level splits into three *fine-structure* levels due to spin-spin interaction; we study the broadening of the j=1 → j=0 *fine-structure* transition, occurring within the first rotational level

• By using angular momentum recoupling techniques [1, 2, 3] we separate the O_2 spin from the problem, and solve the Schrödinger equation for the collision of two spin-free particles on the 4-dimensional potential energy surface (PES)







• Our new 4-dimensional O_2-N_2 PES is computed using the (AE)UCCSD(T)-F12b/CBS methodology with aid of the ''AUTOSURF'' code [1, 4]; the Schrödinger equation is solved numerically using our ''BIGOS'' quantum scattering code [5]

• We transform the obtained spin-free scattering matrices back into the representation which include the quantum spin number – we are thus in a position to compute the line-broadening for a purely *fine-structure* transition in the single rotational level

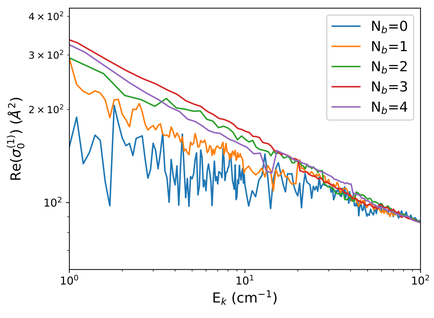
• The ''BIGOS'' code uses the transformed S-matrices to calculate the pressure broadening cross-section for the N_2 perturbation of the j=1 → j=0 *fine-structure* transition in O_2

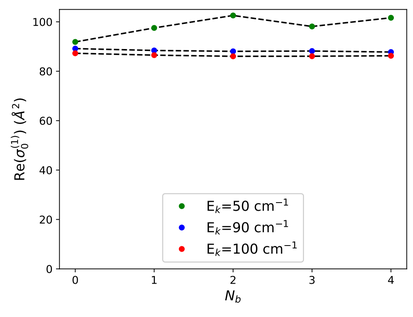
• The energy-averaged cross sections yield the pressure broadening parameter for this line (*i.e.*, the half-width at half maximum, HWHM) as a function of the gas temperature [1]

The results

• We calculated the broadening cross sections in the kinetic energy range from 1 cm^{-1} to ~100 cm^{-1}

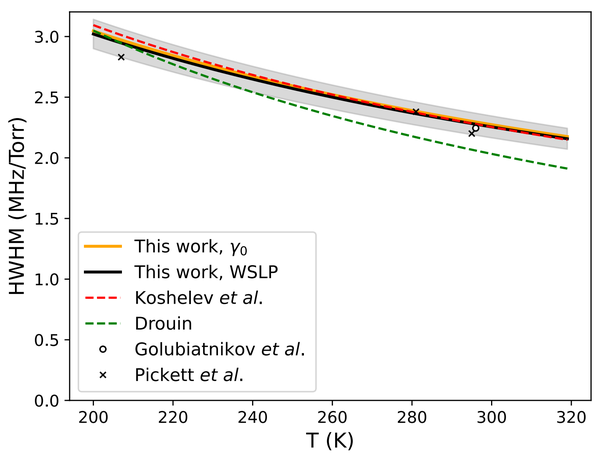
• Here, cross sections are given for first 5 rotational levels of N_2 (labeled with N_b) as a function of kinetic energy; at high enough E_k they become independent of the rotational state of the thermal bath (see the figure on the right)





• We extrapolate the cross sections given in the figure into the higher kinetic energies (up to ~4 000 cm^{-1}); we then assume that for N_2 rotational states with N_b>4, the cross sections are the same as for the N_b=4; thus in the evaluation of the statistical partition sums over bath variables we are able to include the N_2 levels up to N_b=31

• By suitable energy-averaging of the cross sections we obtain both the speed-independent & speed-dependent N_2-broadening coefficients for the O_2 118 GHz line. The temperature dependence of the speed-dependent HWHM is obtained by averaging the speed-dependent Lorentz profiles over the Maxwellian distribution



$$\gamma(T) = \gamma(T_0)\left(\frac{T_0}{T}\right)^{n_\gamma},$$

Experiment	T (K)	γ (MHz/Torr)	n_γ
Pickett *et al.*[19]	207	2.83(6)	···
	281	2.38(5)	···
	295	2.2(1)	···
Golubiatnikov *et al.*[20]	297	2.245(20)	···
Drouin[21]	296	2.06(6)	1.00(5)
Makarov *et al.*[15]	300	2.255(14)	0.79(5)
Koshelev *et al.*[16]	296	2.278(2)	0.781(6)
This work, WSLP	296	2.28(9)	0.7231(1)
This work, γ_0	296	2.30(9)	0.7245(6)

• Our *ab initio* calculations agree with the experimental data (see [1] for the relevant papers) within the estimated 4% uncertainty of numerical calculations (shaded area). This paves the way for more elaborate future analyses of the general line-shape problem for atmospheric O_2 perturbations

Bibliography

[1] Gancewski, M. *et al.* J. Chem. Phys. **155,** 124307 (2021)

[2] Offer, A. R. *et al.* J. Chem. Phys. **100**, 362 (1994)

[3] Corey, G. C. *et al.* J. Phys. Chem. **87**, 2723 (1983)

[4] Quintas-Sánchez, E. e*t al.* J. Chem. Inf. Model. **59**, 262 (2018)

[5] Jóźwiak, H. e*t al.* ''BIGOS computer code'', to be published

Acknowledgements

M.G., H.J., and P.W. were supported by the National Science Centre in Poland through Project No. 2018/31/B/ST2/00720. R.D. and E.Q.-S. were supported by the U.S. Department of Energy (Award No. DE-SC0019740). This project was supported by the French-Polish PHC Polonium program (Project No. 42769ZK for the French part). This project was co-financed by the Polish National Agency for Academic Exchange under the PHC Polonium program (Grant No. dec. PPN/X/PS/318/2018). This research is a part of the program of the National Laboratory FAMO in Toruń, Poland.

Maciej Gancewski
Institute of Physics, Faculty of Physics, Astronomy and Informatics,
Nicolaus Copernicus University in Toruń
ul. Grudziądzka 5, 87-100 Toruń, Poland
e-mail: mgancewski@op.pl