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First-principles calculations of pressure broadening for the case of N₂-perturbed 118 GHz fine-structure line in O₂(X³Σ_g⁻)

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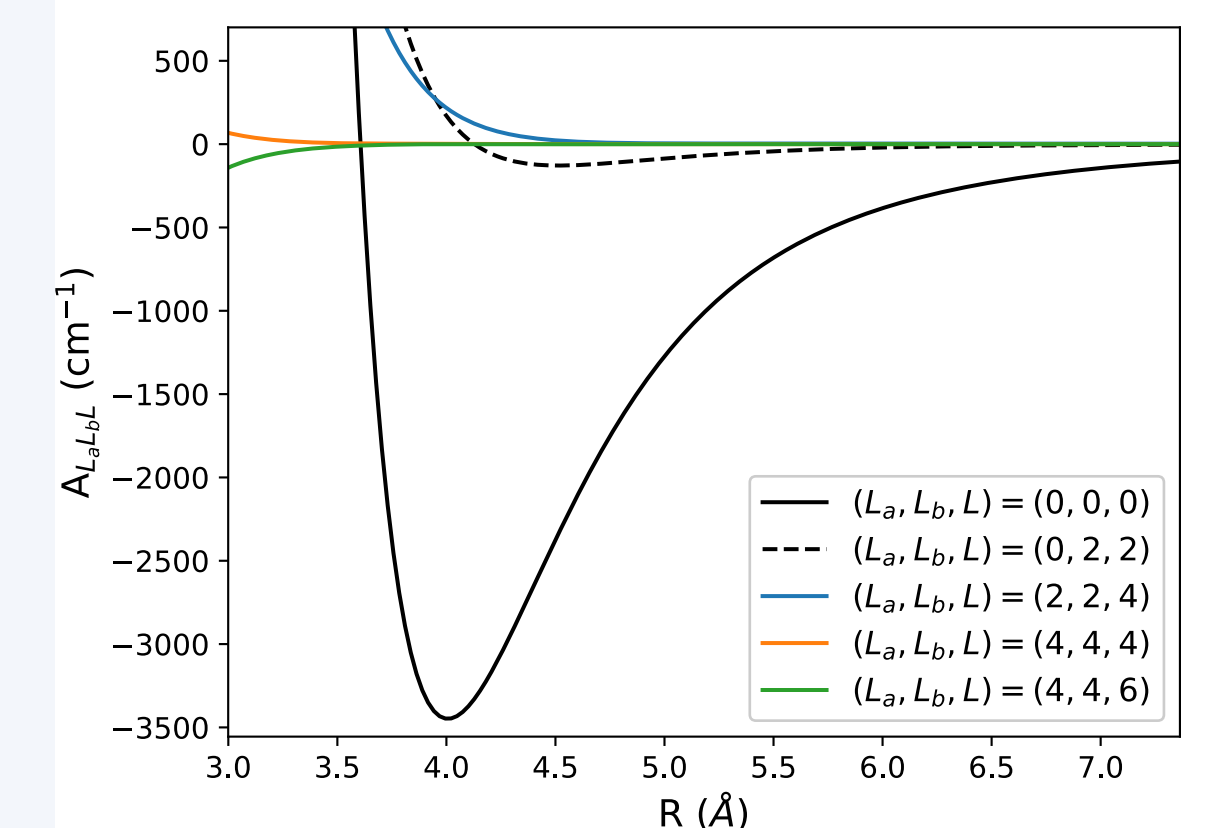
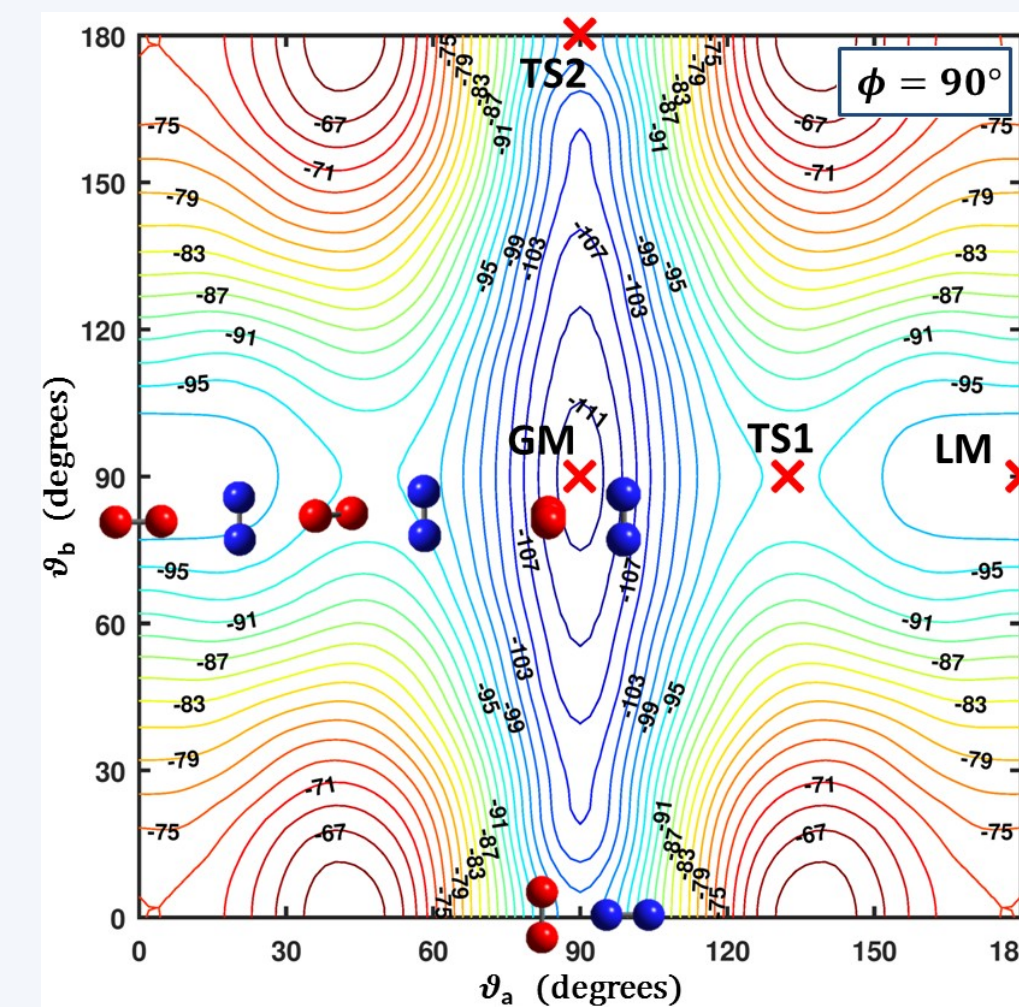
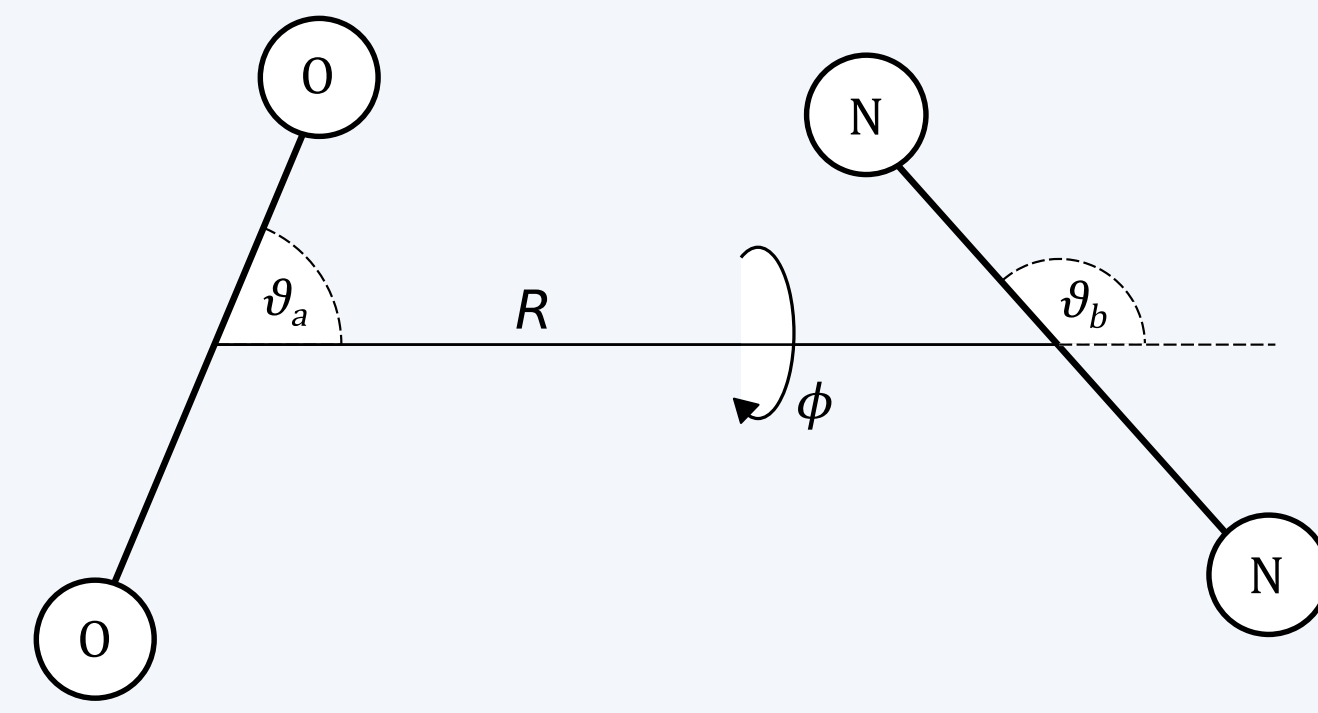
3. Univ. Rennes, CNRS, IPR (Institut de Physique de Rennes)-UMR 6251, Rennes F-35000, France

What is this about?

- The general problem: *How is the absorption (emission) spectrum of O₂ modified when it is immersed in the large bath of N₂ molecules?*
- This model question is important in general considerations of atmospheric physics (~78% of N₂ & ~21% of O₂ 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 O₂ will be affected by its interactions with N₂ in a complicated manner
- A thorough study of these is very challenging (preparation of the potential, solving the Schrödinger & kinetic equations...)
- We thus begin this program by addressing a simpler problem: *How much a single isolated line of O₂ is broadened by collisions with N₂ at different gas temperatures?*
- Here, we consider both (rigid) molecules to be in their ground states & we focus on the N₂-induced perturbations of the isolated fine-structure line (centered at ~118 GHz) of O₂(³Σ)

Our methodology

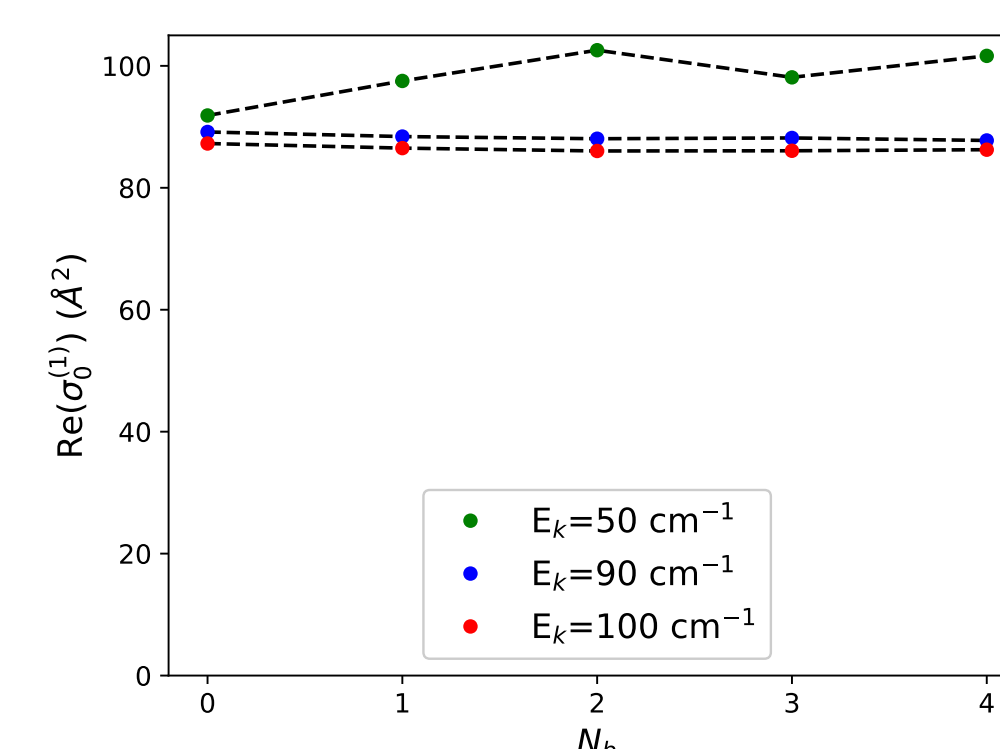
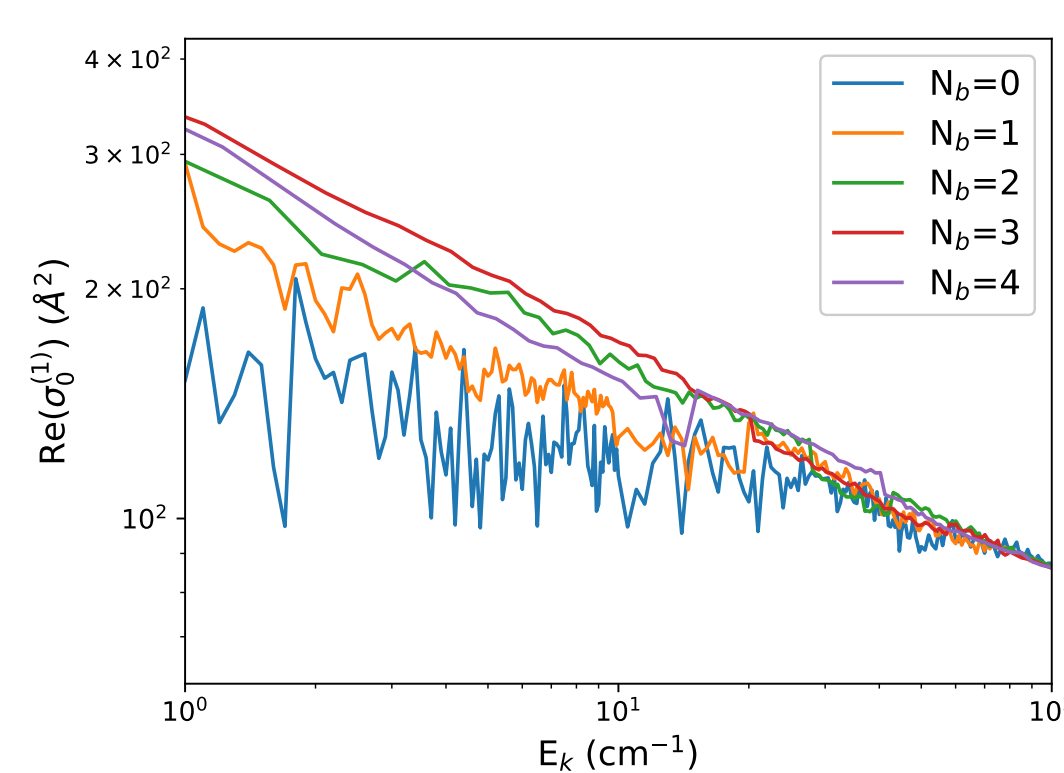
- In O₂(X³Σ) each rotational level splits into three fine-structure levels due to spin-spin interaction; we study the broadening of the $j=1 \rightarrow j=0$ fine-structure transition, occurring within the first rotational level
- By using angular momentum recoupling techniques [1, 2, 3] we separate the O₂ 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 O₂-N₂ 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 N₂ perturbation of the $j=1 \rightarrow j=0$ fine-structure transition in O₂
- 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]

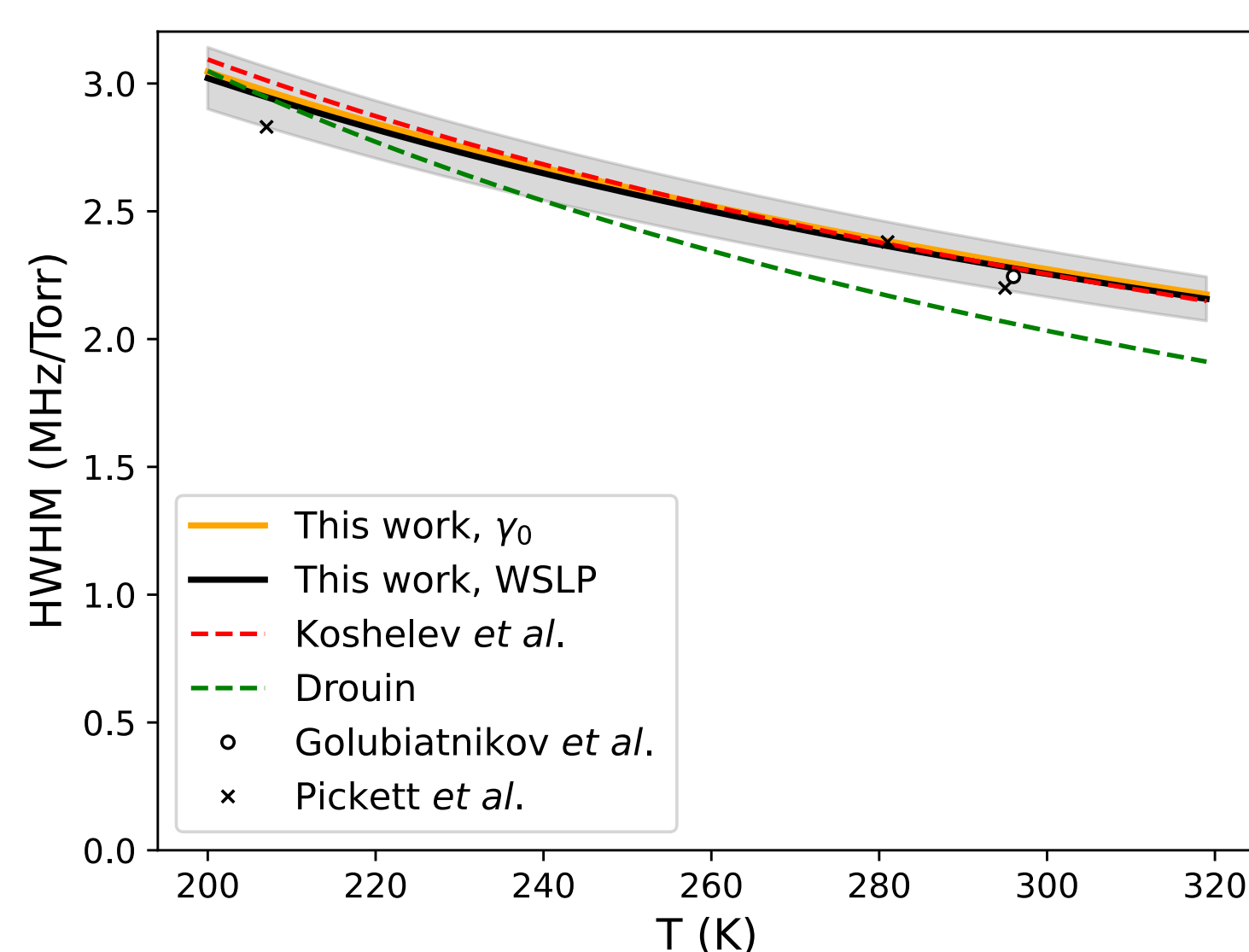
The results

- 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 N₂ (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 N₂ 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 N₂ levels up to N_b=31

- By suitable energy-averaging of the cross sections we obtain both the speed-independent & speed-dependent N₂-broadening coefficients for the O₂ 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 <i>et al.</i> ¹⁹	207	2.83(6)	...
	281	2.38(5)	...
	295	2.2(1)	...
Golubiatnikov <i>et al.</i> ²⁰	297	2.245(20)	...
Drouin ²¹	296	2.06(6)	1.00(5)
Makarov <i>et al.</i> ¹⁵	300	2.255(14)	0.79(5)
Koshelev <i>et al.</i> 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 O₂ perturbations

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