

Comprehensive *Ab Initio* Calculations of CO₂–H₂ and CO₂–He Collisional Properties

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ABSTRACT

We present comprehensive *ab initio* calculations of CO₂–H₂ and CO₂–He collisional properties from first principles, employing CCSD(T), potential calculations together with close-coupling dynamical scattering in the YUMI framework. We derive (in)elastic cross sections, rate coefficients, and pressure-broadening parameters—including, their rotational dependence up to $|m| = 50$, and temperature dependence over the range of 100–800 K. We provide Padé fits for the broadening coefficients as a function of rotational quantum number, enabling extrapolation of the results and integration into spectroscopic databases, including HITRAN and HITEMP. The computed potentials for both CO₂–H₂ and CO₂–He have a sub-percent precision, and the dynamics-solving code YUMI ultimately yields the collisional parameters. Among these, the scaled pressure broadening experimental values meet the 10% precision requirement for exoplanetary sciences with *JWST*. This contrasts with the parameters available before the present calculations, which at higher temperatures ($T > 400$ K) deviate as much as $5\times$ from the desired precision requirement. All derivations and collisional properties are provided with this manuscript, establishing the first of such a comprehensive *ab initio* foundation for collisional systems with a target molecule having more than two atoms.

Keywords: Spectral line lists (2082); Laboratory astrophysics (2004); Infrared spectroscopy (2285); James Webb Space Telescope (2291);

1. INTRODUCTION

CO₂–H₂ and CO₂–He collisional systems have a wide range of applications. As the primary source of carbon reservoir and a strong absorber, CO₂ have been detected with *JWST* in increasing numbers of exoplanets of all sizes and temperatures (Fu et al. 2025). Con-

straining the amount of CO₂ is a powerful diagnostic to inform the formation and evolution history of an exoplanet (Öberg et al. 2011), a task that hinges on accurate determination of its collisional properties. Similarly, the Global Circulation models governing the climates of these exoplanets are sensitive to the collisional properties of CO₂ (Chaverot et al. 2023). For gas and ice giants in the solar system, CO₂ is not abundant but remains an important tracer for atmospheric processes and external material delivery (Feuchtgruber et al. 1997). Similarly, CO₂ is often found in abundance in protoplanetary disks (Bosman et al. 2017; Grant et al. 2023;

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Frediani et al. 2025). Naturally, this system is of interest beyond astrophysics, lying at the center of remote-sensing applications for fields ranging from combustion and the petrochemical industry to medicine.

As data quality improves, so does the expectation of the scientific inferences expected from it. The latter increasingly depends on the quality of the opacity models at the end to interpret the data, more so than on the instrument acquiring the data. In the context of exoplanetary sciences, for example, Niraula et al. (2022) showed that current limitations in our line shape parameters (broadening and far-wing behaviors) impose significant accuracy bottlenecks on our ability to characterize exoplanetary atmospheres. Unfortunately, broadening parameters for many relevant collisional systems are still lacking (Tan et al. 2022). Experimental avenues require substantial funding, a large workforce, and time commitments (Fortney et al. 2016). Moreover, some of the experiments, including $\text{CO}_2\text{-H}_2$ at elevated temperatures, are non-trivial or simply dangerous. To address this gap, we demonstrated an alternative *ab initio* first principle-based computational approach in Wiesenfeld et al. (2025) targeting a single transition of $\text{CO}_2\text{-H}_2$, the only transition with experimental values available at different temperatures (Hanson & Whitty 2014).

Here, we expand upon Wiesenfeld et al. (2025) and perform a comprehensive calculation for the collisional properties of $\text{CO}_2\text{-H}_2$ and $\text{CO}_2\text{-He}$. The latter system is substantially better studied than $\text{CO}_2\text{-H}_2$ both experimentally and theoretically (see, for instance, Korona et al. (2001), but is still important to benchmark our calculations. In Wiesenfeld et al. (2025), we determined the precision requirement to power *JWST* exoplanet studies as a $\leq 10\%$ precision on pressure-broadening coefficients. Each step in our framework is carefully designed to support this goal. With this framework, we compute ro-vibrational transitions up to $|m| = 50$ (that is $j' = 45$, $j'' = 44$) (see section 5), and temperatures spanning from 100 K to 800 K, and derive the pressure-broadening dependence on the rotational quanta and the temperature.

We introduce key definitions, the state of the art (SotA), and our framework in section 2, a summarized theory of collisional properties in section 3, and our methods in section 4. We present our results in section 5, compare them to experimental values in section 6. Concluding remarks are offered in section 7.

2. DEFINITIONS, SOTA, & FRAMEWORK

By *ab initio*, we mean here that the only inputs of our calculations are molecular structures and con-

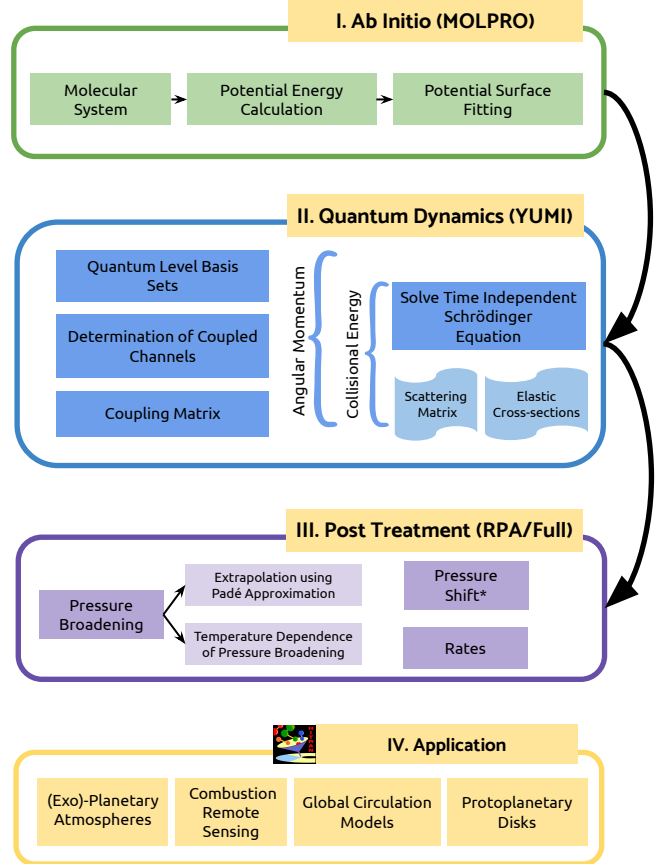


Figure 1. Schematics of the deployed framework for calculating collisional properties of $\text{CO}_2\text{-He}$ and $\text{CO}_2\text{-H}_2$. Various collisional properties of CO_2 by H_2 and He are estimated, which is useful for a wide range of applications, including exoplanetary retrievals. *The calculation of pressure shift is deferred to follow-up work.

stants: the average geometry of CO_2 and H_2 molecules in their relevant vibrational levels and their corresponding rotational constants. All other quantities are computed, including electronic structures of the $\text{CO}_2\text{-H}_2$ and $\text{CO}_2\text{-He}$ van der Waals complexes (see subsection 4.2), and all dynamical quantities (elastic and inelastic cross sections, transfer of population rates, pressure broadening rates, see section 5). An overview of the computational framework is presented in Figure 1. YUMI is our primary in-house code for performing dynamical calculations, which will be described in detail in an upcoming paper (Nejmeddine et al., in prep.).

This framework may be compared to the commonly used approach in the literature for the *ab initio* computation of inelastic scattering. Inelastic cross sections are used for the interpretation of spectral intensities and properties of interstellar matter, especially for rotational spectra (Goldsmith & Langer 1999). Numerous

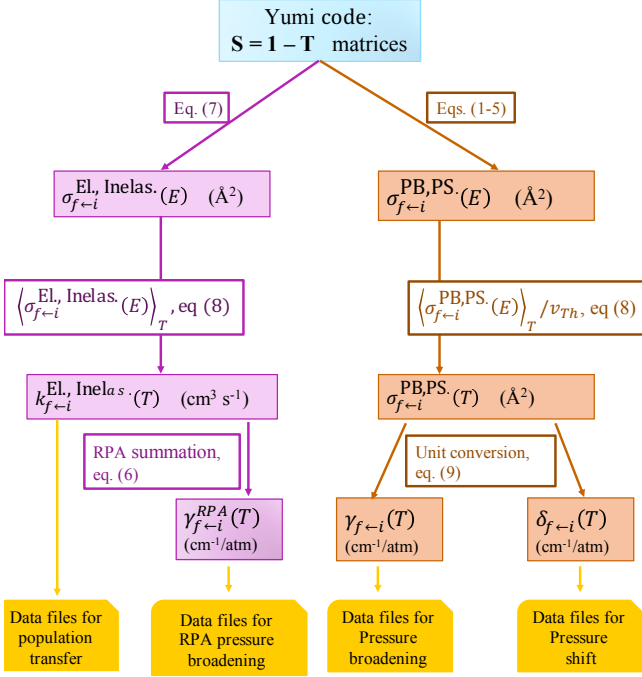


Figure 2. Details of the computational flow for the post-treatment following the dynamics calculation with YUMI.

studies have used *ab initio* methodologies (for example see: van der Tak et al. 2020; Arthurs & Dalgarno 1960; Valiron et al. 2008; Dubernet et al. 2013; van der Tak et al. 2020; Dubernet et al. 2005; Sahnoun et al. 2018; Kowzan et al. 2020; Bergeat et al. 2020; Drouin & Wiesenfeld 2012; Paredes-Roibas et al. 2023; Alexander et al. 2023; Selim et al. 2023). This large body of literature uses the same type of *ab initio* approach, though their specific goals differ widely from our current focus, in terms of precision, temperature range and type of cross-sections (see Appendix C). Inelastic cross-sections and transfer of population rates are necessary for evaluating spectral line intensities for fairly common conditions in the interstellar media (critical density $n^*(\text{H}_2) \sim 10^{4-6} \text{ cm}^{-3}$, temperatures $T \sim 5-300 \text{ K}$). However, the precision needed for interstellar studies is modest, as even a 50% error on the rates remains acceptable. This contrasts sharply with the stringent precision required here, i.e 10% (Wiesenfeld et al. 2025).

In addition, some pressure-broadening computations have been computed *ab initio* akin to ours, with publicly available codes (like MOLSCAT – Hutson & Le Sueur (2019)). In particular, Thibault et al. computed several pressure broadening of molecules by either He or rare gases, (see Thibault et al. 2001, 2012, 2024). Most of these calculations compare favorably with the experimental results, especially so in the intermediate temperature ranges ($T \sim 300 \text{ K}$). The group from Torun has

been carrying out fully *ab initio* calculations targeting a very high level of precision to obtain non-Voigt parameters (e.g. Kowzan et al. (2020); Olejnik et al. (2023); Jóźwiak et al. (2024)) for gases of atmospheric interest, but the targeted sub-percent precision allows calculation of only a few transitions at a time. We computed pressure broadening (and shifts) for H_2O in collision with H_2 at low temperatures ($T \lesssim 100 \text{ K}$), and compared those with experimental results. Despite experiments’ difficulty, excellent agreement was found between them and *ab initio* theory (Drouin & Wiesenfeld 2012).

Several approaches have been used to model pressure broadening, including approximate methods that can handle dynamically intricate cases. A comprehensive review, including different formalisms, has been given by Hartmann et al. (2021). Classical models, in particular, have been used for many years to provide order-of-magnitude estimates of pressure broadening, and in some instances, where empirical corrections are possible, reliable predictions are possible such as for C_2H_2 broadened by H_2 (Sokolov et al. 2025). Classical (requantized) molecular dynamics simulations have also been successful (see, for instance, Ngo & Tran (2025)).

3. ON PRESSURE BROADENING AND SHIFT

We present here a condensed theory of pressure broadening and pressure shift (PB/PS) coefficients, including the relevant approximations. Although the theory has long been established, multiple formulations of the equations exist, and we therefore find it useful to clarify the specific approach we adopt here. Early quantum derivations, still in use, can be found in Baranger (1958); Ben-Reuven (1966); Green (1977); Schaefer & Monchick (1987). A comprehensive analysis together with different approximations, as well as several extensions of the theory, can be found in Hartmann et al. (2018).

Here we make explicit use of the (i) impact approximation, (ii) the isolated line approximation, and (iii) isolated events approximation, (Hartmann et al. 2018). The impact approximation supposes that the duration of the collision is so short that no dynamics of both target and projectile occur *within* the time of the existence of the complex. Isolated line approximation excludes both line mixing, whether through broadening of shift, and the transfer of intensity between the transitions. Although carbon dioxide is notorious for having strong line mixing in the Q-branches of the “perpendicular” bands, including the bending fundamental, these are narrow features and not present in the asymmetric stretch fundamental, which has been identified

on exoplanets so far. Moreover, there are ways to approximately estimate first-order line mixing using energy power gap (EPG) approximation, as it was done for air and self-broadened values in Hashemi et al. (2020). Isolated events allow for collisions to always be two-body events, in distinct succession; no three-body events are taken into account. This latter approximation holds, in practice, up to approximately 1 amagat density for the gas (number density of one standard atmosphere, at 0 °C; it amounts to $\approx 2.687 \times 10^{19} \text{cm}^{-3}$).

Let $\sigma^{\text{PB}}(E)$ be the pressure broadening cross section as a function of E , the collision energy, and let $\sigma^{\text{PB}}(T)$

be the average of $\sigma^{\text{PB}}(E)$ over the Maxwellian distribution of the collision energy E (energies are defined in the Appendix, section Appendix A). A complete derivation of the pressure broadening (PB) and pressure shift (PS) cross sections is found in the seminal papers Ben-Reuven (1966); Coombe et al. (1975).

Here, we present a condensed version of the *energy-dependent* PB and PS cross section. The full case (with $j_2 \geq 0$) is presented in the following equation:

$$\sigma_{j_1' \leftarrow j_1}^{\text{PB;PS}}(E) = \frac{\pi}{k^2} N(j_1'', j_1', j_2') \sum_{q'', q', \bar{q}', \bar{q}'', j_2'', J, \bar{J}} X(j_1'', j_1', q'', q', \bar{q}', \bar{q}'', J, \bar{J}) \left[\langle q'' j_1'' j_2'' | \mathbf{T}^{*J}(E) | \bar{q}'' j_1'' j_2'' \rangle \langle q' j_1' j_2' | \mathbf{T}(E)^{\bar{J}} | \bar{q}' j_1' j_2' \rangle \right]. \quad (1)$$

Pressure broadening and shift are respectively real and imaginary parts of the $\sigma_{q'' j_1'' \leftarrow j_1' q'}^{\text{PB;PS}}(E)$ complex number. $k = \sqrt{2\mu E}/\hbar$ is the wavenumber of the complex at collision energy E , reduced mass μ . j_1' and j_1'' denote respectively the initial and final rotational angular momentum of CO₂. $\mathbf{T}(E) = \mathbf{1} - \mathbf{S}(E)$ is the transition matrix, with $*$ denoting complex conjugation. q' and q'' are collectively the quantum numbers that define the quantum states of combined CO₂ and H₂ molecules (except for levels j_1', j_1'', j_2' , explicitly mentioned), and $J, \bar{J}$ are the total angular momenta of the collision. $N = \tilde{N}/(2j_2' + 1)$ is the normalization, to be discussed in subsection C.3 and Equation 3. It takes into account the degeneracies of the incoming projectile and target.

The important points to observe in Equation 1 are: (i) both brackets in the equation (1) are elastic transitions, that is, the internal states of the observed molecule CO₂ do *not* change in the interaction and (ii) both interac-

tions occur at the same kinetic energy, but different total energies $E_{\text{tot}} = E + E_{\text{internal}}$.

The $X(j_1'', j_1', q'', q')$ coefficients are derived by integrating the differential amplitude of scattering over the spherical angles and using the form of the rotational eigenfunctions. They *do not depend* on the vibrational quantum states, thereby justifying our neglect of the vibrational dynamics, except for the symmetry associated with them subsection 4.1. Full formulae can be found in Schaefer & Monchick (1987); Coombe et al. (1975). We expand the quantum numbers: $q \equiv (j_2, \ell, j_{12})$, where ℓ is the orbital quantum number (the angular number of the projectile with respect to the target center-of-mass) and j_{12} is the recoupling of j_1 and j_2 , see section A for detailed descriptions. We use this form, which we verified to be exactly equivalent to other definitions, thanks to the invariance properties of 6- j symbols:

$$X(.) = P(\ell' + \ell'' + j_{12}' - j_{12}'' + j_{12}' - j_{12}'' + j_1' - j_1'' + j_2' - j_2'') [J_1 J_2] \left[j_{12}' j_{12}'' \bar{j}_{12}' \bar{j}_{12}'' \right]^{1/2} \times \left\{ \begin{matrix} \bar{J} & J & Q \\ j_{12}' & \bar{j}_{12}' & \ell' \end{matrix} \right\} \left\{ \begin{matrix} \bar{J} & J & Q \\ j_{12}'' & \bar{j}_{12}'' & \ell'' \end{matrix} \right\} \left\{ \begin{matrix} j_1'' & j_1' & Q \\ j_{12}' & \bar{j}_{12}' & j_2' \end{matrix} \right\} \left\{ \begin{matrix} j_1'' & j_1' & Q \\ j_{12}'' & \bar{j}_{12}'' & j_2'' \end{matrix} \right\} \quad (2)$$

where $P(q) = (-1)^q$ and $[JJ'] = (2J+1)(2J'+1)$. Q is the multipolar order of the electromagnetic transition. Here $Q = 1$, for dipolar transition. Note that $\ell' = \bar{\ell}'$ and $\ell'' = \bar{\ell}''$. The normalization and angular recoupling

schemes (Eq. (1), Eq. (2)) are valid for any collision rotator - atom or rotator - rod, as the supplementary quantum numbers k or τ for resp. symmetric or asymmetric rotors are spectators in the recoupling scheme

presented in [Appendix A](#). However, for the rotor/rotor (e.g., like water-water collisions) $X(\cdot)$ coefficients are different, as the projectile rotational eigenfunctions in the lab. frame will entail full Wigner rotation functions (see e.g. [van der Avoird et al. 1994](#)). Noteworthy is the appearance of the $g(q')$ denominator ($g = 1/(2j_2' + 1)$ for a rod), as the degeneracy of initial conditions in the spectator projectile must be taken into account, see ([Green 1977](#); [Drouin & Wiesenfeld 2012](#)). One must also ensure that the $\sigma_{j_1'' \leftarrow j_1'}^{\text{PB;PS}}(E)$ sections are independent of the

order $i \leftrightarrow f$, and so, adapt the degeneracies included (or not) in the $\mathbf{T}$ matrices computations, [subsection C.3](#) and [Equation 5](#).

Also, in the case of helium or para- H_2 , $j_2 = 0$ (no structure of the projectile), [Equation 1](#), [Equation 2](#) simplifies thanks to the properties of the Wigner 6-j symbols, yielding an equivalent expression to Eq. (A4) in [Thibault et al. \(2001\)](#):

$$\sigma_{j_1'' \leftarrow j_1'}^{\text{PB;PS}}(E) = \frac{\pi}{k^2} \tilde{N}(j_1', j_1'') \sum_{q'', q', \bar{q}'', \bar{q}', J, \bar{J}} X(j_1'', j_1', q'', q', \bar{q}'', \bar{q}'; J, \bar{J}) \langle q'' j_1'' | \mathbf{T}^{*J}(E) | \bar{q}'' j_1'' \rangle \langle q' j_1' | \mathbf{T}(E)^{\bar{J}} | \bar{q}' j_1' \rangle \quad , \quad (3)$$

with

$$X = (2J + 1)(2\bar{J} + 1) \begin{Bmatrix} j_1' & q & j_1'' \\ \bar{J} & \ell & J \end{Bmatrix} \begin{Bmatrix} j_1' & q & j_1'' \\ \bar{J} & \bar{\ell} & J \end{Bmatrix} \quad (4)$$

and

$$\tilde{N} = \sqrt{\frac{2j_1^< + 1}{2j_1^> + 1}} \quad , \quad (5)$$

for absorption lines, with $j_1^>$ (resp. $j_1^<$), the larger and the smaller of the two connected j_1 levels, see [subsection C.3](#). The scattering matrices $\mathbf{S}$ are related to the transfer matrices $\mathbf{T}$ by $\mathbf{S} = \mathbf{1} - \mathbf{T}$.

In addition to the above formulae, the use of the optical theorem allows us to have another view of the PB cross-sections, which is fully equivalent (but not valid for the PS cross-sections) ([Baranger 1958](#); [Faure et al. 2013](#)):

$$\sigma_{j_1'' \leftarrow j_1'}^{\text{PB}}(E) = \frac{1}{2} \left[\sum_{\bar{j}_1 \neq j_1'} \sigma_{\bar{j}_1 \leftarrow j_1'}^{\text{In.}}(E) + \sum_{\bar{j}_1 \neq j_1''} \sigma_{\bar{j}_1 \leftarrow j_1''}^{\text{In.}}(E) \right] + \int |f_{j_1'}(E, \Omega) - f_{j_1''}(E, \Omega)|^2 d\Omega \quad , \quad (6)$$

where $\sigma_{\bar{j}_1 \leftarrow j_1'}^{\text{In.}}(E)$ are ordinary inelastic cross sections, $f_{j_1'}(E, \Omega)$ are elastic differential scattering amplitude, and Ω is the solid angle of scattering. The second term, which describes interferences between incoming and outgoing scattering wavefunctions, may be neglected (the Random Phase Approximation (RPA)) at higher energies, when forward scattering dominates the dynamics and phase differences oscillate rapidly, therefore goes to zero when averaged over a Maxwellian distribution of kinetic energies. We pursue both approaches in this work, [Eq.\(1\)](#) and [Eq.\(6\)](#), and test their validity.

In order to be complete, the ordinary cross sections, elastic or inelastic, are defined as:

$$\sigma_{f \leftarrow i}(E) = \frac{\pi}{k^2} \frac{1}{g_i} \sum_{qq'} (2J + 1) |\langle f q' | \mathbf{T}^J | i q \rangle|^2 \quad (7)$$

where i and f are quantum numbers of initial and final levels (in all generality), q , q' are the other quantum numbers describing the couplings of the various states, g_i is the degeneracy of the initial level depending on the type of section that we are interested in (see [Eq.\(12\)](#) in [Green \(1975\)](#)), and k is as in [Eq.\(1\)](#).

The temperature-dependent average section (in $\text{\AA}^2$) and the pressure broadening coefficient $\gamma(T)$ (in wavenumber/atmosphere, for Half Width at Half Maximum) are defined as:

$$\sigma_{j_1'' \leftarrow j_1'}^{\text{PB;PS}}(T) = k_{j_1'' \leftarrow j_1'}^{\text{PB;PS}} / v_{\text{Th}} \quad (8)$$

$$\gamma = k_{j_1'' \leftarrow j_1'}^{\text{PB}} / 2\pi k_B T = \sigma^{\text{PB}}(T) v_{\text{Th}} / 2\pi k_B T \quad (9)$$

where $k_{j_1' \leftarrow j_1'}(T)$ is the usual rate obtained by averaging $\sigma_{j_1' \leftarrow j_1'}(E)$ over the Maxwellian distribution of E and $v_{\text{Th}} = \sqrt{8k_B T / \pi \mu}$ (μ , reduced mass of the collision):

$$k(T) = \frac{v_{\text{Th}}}{(k_B T)^2} \int_0^\infty \sigma(E) E \exp(-E/k_B T) dE \quad (10)$$

where cross-sections $\sigma(E)$ stand for any type of collisional rate (elastic, inelastic, pressure broadening, pressure shift).

4. METHODS

4.1. Spectroscopy

Although very well known for many years, both the $^{12}\text{C}^{16}\text{O}_2$ and $^1\text{H}_2$ symmetries are relevant to the present work and are discussed here. Both molecules show $D_{\infty h}$ symmetry. ^{16}O has nuclear spin $I = 0$ and ^1H has nuclear spin $I = 1/2$. Both come in two spin modifications. CO_2 , with zero nuclear spin, exists only in the para state (angular momentum $j_1 = 0, 2, \dots$) for the ground vibrational state. For asymmetric vibrational states, such as $v_3 = 1$ (asymmetric stretch), only odd values of j_1 exist. For H_2 , the two spin modifications exist regardless of the vibrational state. Para states (singlet total nuclear spin state $I = 0$) have even j_2 angular momentum, ortho states (triplet total nuclear spin states, $I = 1$) have odd angular momentum j_2 .

We suppose that the vibrational dependence of pressure broadening is minimal for CO_2 , as is experimentally demonstrated for collisions of CO_2 with air (Hashemi et al. 2020). Since the ν_3 band transitions connect levels with $\Delta j_1 = \pm 1$ (P and R branches, no Q branch for the band we look at, but can be estimated based on P and R branch values), we need to deal with two different vibrational levels of opposite parity. We considered the vibrational ground state, $v = 0$, and the first asymmetric stretch level, $v_3 = 1$. We made use of the same PES for both levels, neglecting the slight difference that could arise. However, we took into account the difference in rotational constants (see subsection 4.2).

To summarize, the computations goes as follows: (i) select a set of collision energies E_i ; (ii) For each E_i , compute for each value of m (see Appendix A for a definition of m) the total energy (for example, $m = -25 \Rightarrow j_1 = 25$ and $j_1 = 24$ so that $E'_{\text{tot}} = E_i + E_{\text{rot}}(25)$ or $E''_{\text{tot}} = E_i + E_{\text{rot}}(24)$); (iii) conduct dynamics at $E'_{\text{tot}} \Rightarrow \mathbf{T}'(E_i)$ and $E''_{\text{tot}} \Rightarrow \mathbf{T}''(E_i)$. Combine via Eq. (1) or Eq. (3) to get $\sigma^{\text{PB,PS}}(E_i)$.

4.2. Ab initio quantum chemistry

We compute the interaction of CO_2 with the bath species He and H_2 . The following physical parameters (distance in Bohr) were used for bond lengths: $R(^{12}\text{C}^{18}\text{O}) = 2.1944$, $R(^1\text{H}^1\text{H}) = 1.448736$. The CO_2 distance depends very weakly on the vibrational state, so that we did not compute a different PES for CO_2 , in the ground or excited vibrational state. The distance HH corresponds to the average ground state of the H_2 molecule (Valiron et al. 2008).

The CO_2 -He Potential Energy Surface (PES) has been computed in several instances with very similar results. Most PES were computed with both spectroscopy of the complex and scattering in mind (Yang & Stancil 2009; Godard Palluet et al. 2022). The CO_2 - H_2 PES has been computed only in a few instances (Li et al. 2010), and the existing PES does not fully meet the requirements of the present work. We, therefore, recompute both PES in an identical fashion.

We employed the so-called Golden Approximation to compute the Born-Oppenheimer PES (Kodrycka & Patkowski 2019). At the level of precision required – about one wavenumber at the bottom of the PES well – the CCSD(T) method was adopted. This choice reflects the method’s versatility, wide usage in the literature, and balanced trade-off between computational time and accuracy (Jeziorska et al. 2008; Varandas 2018). In particular, we adopted the option of using the CCSD(T) functional, without the F12 approximation to the electron-electron short-range interaction, because of well-known problems at large intermolecular distances. Instead, we took the slightly more expensive approach of using both mid-bond atomic basis sets (Shaw & Hill 2018) and a standard Complete Basis Set extrapolation scheme Kodrycka & Patkowski (2019). The basis sets used are aug-pVXZ Werner et al. (2010), most appropriate for molecules comprising light elements with long-range interactions. We used X values of 3, 4 and, for a reduced set of configurations, X = 5 and 6. We checked that the 3-4 and 4-5 extrapolation schemes are equivalent at the level of precision necessary here. The mid-bond point was situated at half distance between the center of mass of the projectile and the nearest atom of the target, thereby avoiding mid-bond functions that could strongly overlap with target ones.

For computing the interaction energy and building the PES, we used the super-molecular approach, corrected for the Basis-Set-Superposition-Error (Kodrycka & Patkowski (2019), see Wiesenfeld et al. (2025) for a method description, and Jeziorska et al. (2008); Varan-

das (2018) for the CBS/BSSE formalism). We have:

$$E^{\text{Int.}}(AB) = E_{AB}(AB) - E_{AB}(A) - E_{AB}(B) \quad (11)$$

where A and B denote atomic bases centered on fragments A and B, respectively. The influence of the compound electronic basis set AB is thus taken into account in the same way when computing the electronic energies of the A fragment, the B fragment, and both A and B fragments interacting.

A few effects are neglected in this approach, that could be of importance as the collision energy increases, such as: (i) the rigid body approximation, that neglects the deformation of fragments as they approach one another; (ii) neglect of any non Born-Oppenheimer effects, such as possible electronic excited levels contamination of the ground electronic level considered here. Point (i) is in line with the impact approximation for the PB formalism. Since all elements are light, no relativistic models of the atoms are necessary, as admitted for elements of the first lines (up to Ne, and even Ar).

The $\text{CO}_2\text{-He}$ PES potential $V(r, \theta)$ depends on 1 angle (the polar angle $0 \leq \theta < \pi$) and on the r distance between atoms C and He. It makes the computation very economical. We resorted to $n_\theta = 41$ angles (randomly distributed over $0 \leq \theta \leq \pi$), not enforcing the symmetry to have a more robust fit. The random distribution has the advantages of (i) being resonance free for all orders of Legendre polynomials $P_l(\cos \theta)$, as long as $l < 41/2$,

and (ii) being able to add points if judged necessary to ensure a good fit. We computed the potential $V(r, \theta)$ for 43 distances, $3.50 \leq r \leq 50$, with steps representative of the variation of V . In total, $N \lesssim 2000$ points were computed. The resulting PES is compared to earlier computation from Godard Palluet et al. (2022).

The $\text{CO}_2\text{-H}_2$ PES depends on 3 angles (Two polar angles $0 \leq \theta_{1,2} < \pi$ and one dihedral angle $0 \leq \phi \leq \pi/2$). We also resorted to a random distribution of the 3 angles, to which we added the special orientations $(\theta_1, \theta_2, \phi) = (0, 0, 0; 0, 90, 0; 0, 90, 90)$ degrees. Wiesenfeld et al. (2025) discusses in detail the PES.

4.3. Fit

Both PES were fit on the usual base suitable for scattering computations (Valiron et al. 2008; Hutson & Le Sueur 2019). The formalism is essentially the same for any scattering involving a target and an atom or a rod. The usual formalism follows Green (1977):

$$V(R, \Omega) = \sum V_q(r) A_q(\Omega) \quad (12)$$

where Ω represents the angles setting the orientation of the projectile (here He or H_2) with respect to the target (CO_2), and q refers to the appropriate orders of the fitting functions.

For a H_2 projectile, we have the following expression Green (1977), compatible to our definitions of Legendre $P_l(\cos \theta)$ and associated Legendre functions $\mathcal{P}_\ell^m(\cos \theta)$ (see subsection C.2):

$$A_{\ell \ell_1 \ell_2}(\theta_1, \theta_2, \phi) = \sqrt{\frac{2\ell+1}{4\pi}} \left[(-1)^{\ell_1-\ell_2} \begin{pmatrix} \ell_1 & \ell_2 & \ell \\ 0 & 0 & 0 \end{pmatrix} P_{\ell_1}(\cos \theta_1) P_{\ell_2}(\cos \theta_2) \right. \\ \left. + \sum_{m>0} 2(-1)^{m+\ell_1-\ell_2} \begin{pmatrix} \ell_1 & \ell_2 & \ell \\ m & -m & 0 \end{pmatrix} \mathcal{P}_{\ell_1}^m(\cos \theta_1) \mathcal{P}_{\ell_2}^m(\cos \theta_2) \cos(m\phi) \right] \quad (13)$$

with angles as in Figure B1. $\begin{pmatrix} \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \end{pmatrix}$ are 3-j symbols.

Eq. (13) simplifies if the projectile is an atom ($m \equiv 0$, $\ell_2 \equiv 0$, $\ell_1 = \ell$) and we have:

$$A_{\ell_1}(\theta) = P_{\ell_1}(\cos \theta), \quad \ell_1 = 0, 2, \dots \quad (14)$$

with $P_{\ell_1}(\cos \theta)$, the Legendre polynomials. Normalization of the Legendre polynomials and the associated Legendre functions $\mathcal{P}_\ell^m(\cos \theta)$, is described in subsection C.2. Both forms are used in the YUMI code.

4.4. Dynamics

We solve the time-independent Schrödinger equation in the Space-Fixed (SF) reference frame. The Potential Energy Surface (PES) described in subsection 4.2 and fitted as described in Appendix B, $V(r, \Omega)$, is the PES introduced in the Schrödinger equation describing the motion of the projectile with respect to the target.

The equations to solve are the Close-Coupling equations (CC) (named Coupled Channels in some litera-

ture), as described by [Arthurs & Dalgarno \(1960\)](#); [Green \(1977\)](#). These equations are coded into the YUMI code, with distinct implementations corresponding to the various geometrical cases (similar to the MOLSCAT code, but with a fully modular construction).

With the definition of the expansion as in [Equation 13](#), the matrix elements of the potential coupling between the states is an algebraic closed formula (Eq.(9) from [Green \(1975\)](#)), obtained by integrating the $A_{\ell_1 \ell_2 \ell}(\theta_1, \theta_2, \phi)$ functions over the angles of both rotator eigenfunctions.

The main numerical task is thus to integrate the Schrödinger equation in the radial coordinates (the CC equations). In order to allow for the stability of the numerical procedure, radial equations are solved by means of a Riccatti equation, for the log-derivative of the $Y_q(r) = \psi'_q(r)/\psi_q(r)$ functions. The T or S matrices are determined by matching the relevant Y_q to the spherical regular or irregular Bessel functions, in the asymptotic region ([Johnson 1973](#); [Manolopoulos 1986](#)).

The strategy is to compute the S-matrices for as few kinetic energies as possible, but still enough to have a good description of the scattering and with sufficiently high E to describe the higher temperatures, high j_1 cases with reasonable precision. Following [Wiesenfeld et al. \(2025\)](#), we target a convergence at a 5%-precision level.

We optimized the computational procedure and the energy/angular parameters (see [Appendix E](#)). For the higher E cases ($E \lesssim 2000 \text{ cm}^{-1}$), the convergence with total angular momentum J is very slow and a value of $J \sim 120$ is necessary. Similarly, in order to treat the couplings properly, enough CO_2 rotational levels must be included. Closed channels with $E = E_{\text{tot}} - E_{\text{rot}} > -V_{\text{min}}$ must be included; This amounts in practice to adding 3 to 5 closed channels to the basis set.

While for collisions with He and with para- H_2 ($j_2 = 0$) these conditions could be met, convergence for ortho- H_2 ($j_2 = 1$) could not be achieved at $E \gtrsim 500 \text{ cm}^{-1}$. Indeed, the triple degeneracy of the $j_{12} = j_1, j_1 \pm 1$ leads to a ninefold increase in the computational time (see [Appendix E](#)). As j_1 grows, the computational load becomes increasingly prohibitive, making exact CC calculations unfeasible. For practical purposes, computations were limited to $j_1 \leq 44/45$ for collisions with H_2 and $j_1 \leq 54/55$ for collisions with He. We defer a full analysis for the $j'_2 > 0$ cases to follow-up work.

4.5. Post-Treatment

YUMI yields tables of the $\langle f q'' | T^J | i q' \rangle$ matrix elements. These are duly summed to yield the observables needed as shown in Eq.(1), Eq.(3), or Eq.(7). The same procedure had been used for differential cross sections ([Yang et al. 2011](#)), or previous pressure broadening sections ([Drouin & Wiesenfeld 2012](#)).

5. RESULTS

5.1. Potential energy surfaces

Table 1 gives the coordinates and values of the minima of the PES's, and compares those to the existing literature values. One sees that our approach is similar to earlier ones, with errors of the order of a few %, compatible with our precision goal and with differences in methods of earlier works. Indeed, we expect all the neglected effects, in particular non-rigid molecules and non-Born-Oppenheimer perturbations, to be of that order of magnitude, as discussed in the so-called “platinum” approximation ([van der Avoird et al. 1994](#); [Kodrycka & Patkowski 2019](#)).

Table 1. Global minimum values of the $V_{\text{H}_2-\text{CO}_2}$ and $V_{\text{He}-\text{CO}_2}$ potentials. Comparison with the literature. Angles identical for this work and literature references. Distances in Bohr, angles in degrees, potential values in cm^{-1} .

System	Angles			This work		Literature	
	θ_1	θ_2	ϕ	r	E	r	E
H_2-CO_2	90	90	0	5.595	-222.65	5.612	-219.75 (a)
$\text{He}-\text{CO}_2$	90	–	–	5.77	-48.55	5.78	-49.22 (b)

(a) [Li et al. \(2010\)](#) ; (b) [Godard Palluet et al. \(2022\)](#)

Fits (see section 4.3) were performed taking into account the symmetries of both H_2 and CO_2 . For He collisions, $P_{\ell_1}(\cos \theta)$, $\ell = 0, 2, \dots, 12$ were used. For H_2 collisions, we have $\ell_1 = 0, 2, \dots, 24$, $\ell_2 = 0, 2, 4, 6$ and total $\ell \leq 26$, resulting in 158 terms (see Eq. 13). The quality of the fit for the $V_{\text{H}_2-\text{CO}_2}$ PES is discussed in detail in our previous work [Wiesenfeld et al. \(2025\)](#). Actual values are given in the data files ([Appendix D](#)), in a format readable by the YUMI code.

In the radial coordinate r , fits are interpolated for $r_{\text{min}} \leq r \leq r_{\text{max}}$ using cubic spline coefficients. For $r < r_{\text{min}}$, the potential is extrapolated by an exponentially increasing function. For large distance, inverse power functions C_n/r^n , $n \geq 6$ were used for the main terms, with a limit $V > 0.01 \text{ cm}^{-1}$.

The $\text{He}-\text{CO}_2$ PES fit is precise, with an r.m.s. error of $\sim 0.01\%$ between V_{abinit} (see [Figure B2](#)) and V_{fit} . For

the H₂-CO₂ PES fit, an r.m.s. error of 1% is found. Lowering this error requires doubling the number of *ab initio* points, rendering the computation heavy.

As mentioned, all details for the H₂-CO₂ PES may be found in [Wiesenfeld et al. \(2025\)](#), and in particular in the supplementary materials. Suffice to say that the PES with 4 degrees of freedom (1 distance, 3 angles) was obtained in the same formalism as here. The angles were chosen in a globally random fashion ([Rist et al. 1993](#); [Sahnoun et al. 2018](#)),

5.2. Dynamical computation results

As described earlier, [subsection 4.1](#), we need to compute the inelastic and elastic complex matrix elements of $S(E)$ or $T(E)$ matrices. For pressure broadening and shift, only elastic matrix elements have to be computed for collision energies between 10 and 2000 cm⁻¹. For population transfer rates, inelastic elements have to be computed. Previous work on ro-vibrational transitions has shown that, most of the time, inelastic rates are dominated by rotational inelastic, vibrationally elastic rates [Wiesenfeld \(2023\)](#). While this is by no means a general conclusion, it is empirically supported here for CO₂ molecules, as experiments have shown the pressure broadening depends very weakly on the vibration levels considered (< 2%) ([Tan et al. 2022](#)). We thus compute all matrix elements within the ground rotational level, separating the even and odd j_1 into two different series.

5.2.1. Convergence criteria

Convergence of the computations of cross-sections $\sigma_{j_1'' \leftarrow j_1'}^{\text{PB;PS}}(E)$ (Eq. (1)) and associated rates is difficult to ensure, requiring trials and errors for tuning computational parameters such as NSTEPS (see [Appendix C](#)) to carry out dynamical computation, given the scarce literature on the topic. Several parameters are to be set: (i) the total amount of CO₂ rotational levels, which amounts here to the maximum value of j_1 ; (ii) the values of j_2 , describing the rotational dynamics of H₂; (iii) the actual integration parameters for the Riccati scheme (see [Table 2](#)), in particular R_{max} ; (iv) the largest value of total angular momentum J in the sums of equations (1) & (3). Also, [Figure C3](#) shows the J behavior of the convergence for the sums in Eq.(1). Furthermore, in order to converge the rates $k_{f \leftarrow i}(T)$, for $T \lesssim 800$ K, $E \approx 1900$ cm⁻¹ must be reached. We computed the dynamics from $10 \leq E \leq 1900$ cm⁻¹, with steps increasing from 5 to 100 cm⁻¹.

Modeling dynamics with H₂ is way more problematic. For ortho-H₂, limiting to $j_2 = 1$ is a reasonable approx-

Table 2. Extreme values of the convergence parameters. Actual parameters for other cases were given intermediate values. Energies in cm⁻¹.

Parameter	$E = 100; m = 2$	$E = 1900; m = 24$
j_1^{max}	59	75
R^{max}	50	50
J_{max}	70	120

imation, as we *do not* explicitly include ro-vibrational transitions [Drouin & Wiesenfeld \(2012\)](#). In contrast, for para-H₂ an inclusion of the $j_2 = 2$ levels should be investigated. However, the number of coupled states for each $|j_1, j_2, j_{12}\rangle$ level ([Appendix, section A](#)) goes from 1 to 4, resulting in computational effort multiplied by more than one order of magnitude and also hitting the fast memory barrier. Approximation schemes will be needed to overcome this problem for high j_1 , high E computation necessary for precision computations.

5.2.2. Elastic and Inelastic scattering rates

We computed, using [Equation 7](#), the usual population transfer sections and rates, keeping in mind that only j_1 odd/even $\leftrightarrow j_1$ odd/even are computed. Examples of rates (elastic and inelastic) are shown in [Figure 3](#), for para-H₂ ($j_2 = 0$), ortho-H₂ ($j_2 = 1$), and He collisions. As is common, all rates connecting the $j_1 = 0$ level are particular, due the degeneracy of the triangle conditions in the various recoupling 3-j or 6-j symbols appearing in the evaluation of the matrix element in [Equation 7](#).

The full sets of elastic and inelastic rates (in 10¹¹ cm³ s⁻¹) are provided as Supplemental Data in a [Zenodo repository](#), alongside energy levels with respect to $j_1 = 0$ energy level taken at the origin. The rates according to the LAMDA convention ([Schöier et al. 2005](#)), except that the Einstein A coefficients are not included. Recall that we include neither ro-vibrational transfer rates, nor $j_1' \text{ odd} \leftrightarrow \text{odd } j_1''$ transitions. These data could be used in helping to model the spectral lines intensities in the IR region, but with utmost caution, since the rates of the $v'' \leftarrow v'$ transitions and the timescales of the IR transitions are not taken into account, all the more that the purely $v' = v''$ transitions are forbidden for electric dipolar transitions. It is thus somewhat irrelevant to compare results for population transfer rates (Eq.(7)) to literature results. However, a cursory comparison of the data of [Figure 3](#) with those for other rod-like molecules, like CO (small dipole, [Yang et al. \(2006\)](#)), or heavy-heavy diatomic, like SiO ([Balança et al. 2018](#)), shows good plausibility of our present results.

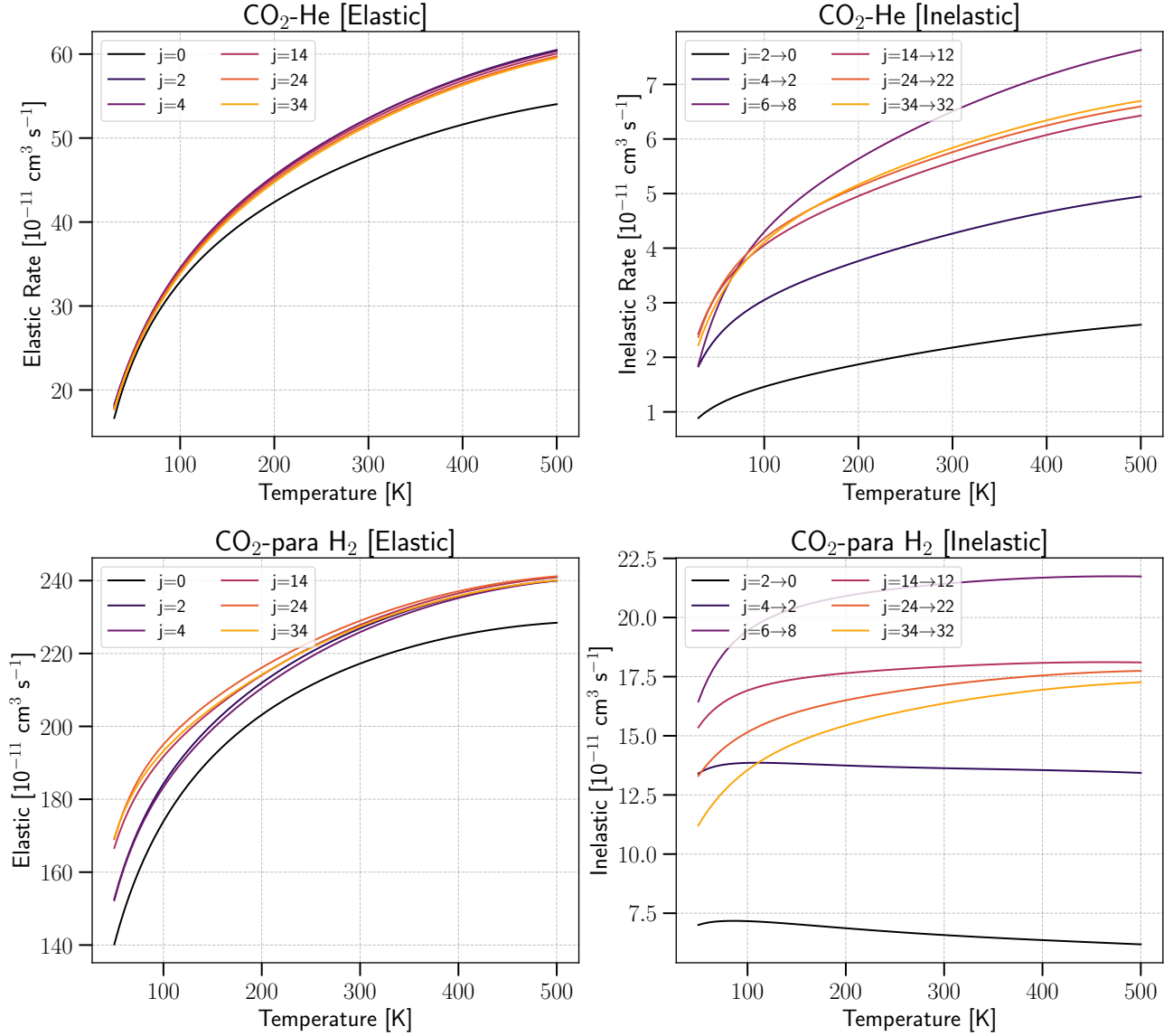


Figure 3. Elastic and inelastic rates $k(T)$ for ground-state CO₂ colliding with He and para-H₂. Elastic rates are roughly an order of magnitude larger than inelastic ones.

5.2.3. Pressure Broadening data

Results—We begin by presenting our results for standard room temperature (296 K) and compare with experiments, in Figure 4. In Table 3, we give the γ values for all transitions ($|m| \leq 50$), for He–CO₂ and H₂–CO₂ collisions, at room temperature (296 K). For collisions with He, we use the full, non-RPA values for $|m| \leq 24$ and the RPA values for $|m| > 24$ (See Figure 2, section 3, and Faure et al. (2013)). Similarly, for collisions with H₂, we present full, non-RPA results (called ‘full’ results) for $|m| \leq 24$ and the RPA values for $|m| > 24$, for collisions with para-H₂. Once scaled (see next paragraph), the main difference stems from the different

slope of $\gamma(|m|)$ function, which is anyhow replaced by the non-RPA values for this range of $|m|$ values.

Scaling—In principle, the theoretical and experimental values of γ should be compared directly, with *no scaling whatsoever*. Doing so, the ratio $\epsilon = \text{theory/experiment}$ for the computations, at $T = 296 \text{ K}$, $|m| = |24|$ are: (i) He collision, for the experimental data of Hendaoui et al. (2025), $\epsilon(\text{He}) = 1.18$ (no approximation) and $\epsilon(\text{He}) = 1.08$ (RPA approx.); (ii) H₂ collisions, for the experimental data of Hanson & Whitty (2014), $\epsilon(\text{H}_2) = 0.97$ (no approximation) $\epsilon(\text{H}_2) = 1.04$ (RPA). Note that both RPA values are largely within the $\pm 10\%$ precision needed for the accurate modeling of planetary atmospheres, (Niraula et al. 2022, 2023; Wiesenfeld et al.

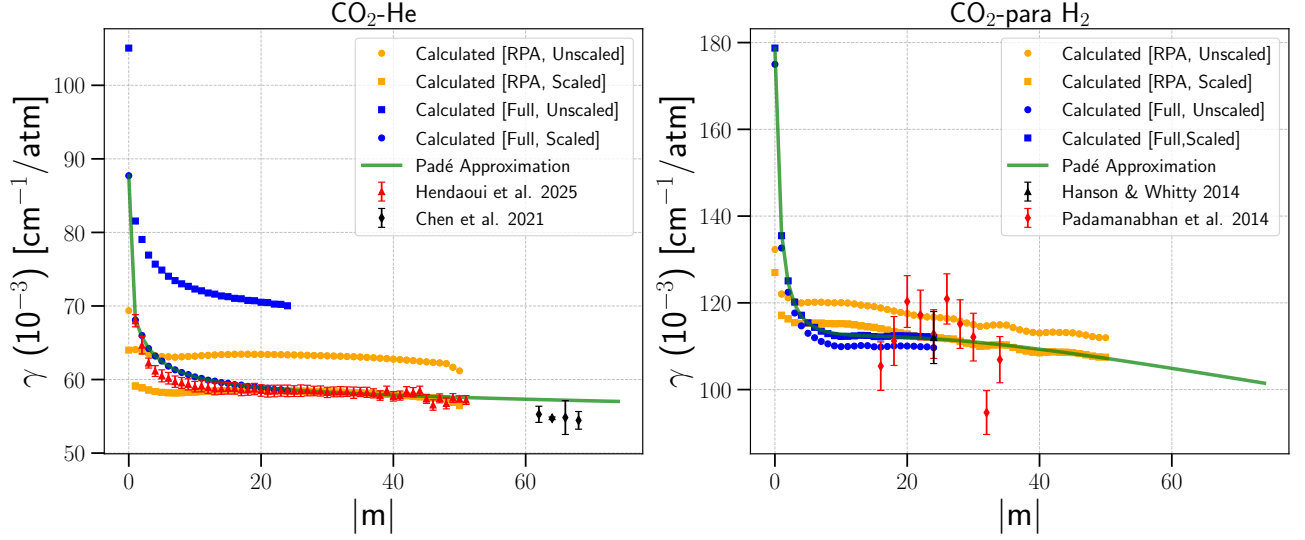


Figure 4. **Left:** Broadening CO₂-He at 296 K as a function of rotational quanta, comparison with experiment. The experimental values are taken from Hendaoui et al. (2025) and Chen et al. (2021), while the Padé approximation are fitted to our scaled calculations. **Right:** Broadening CO₂-para H₂ at 296K as a function of rotational quanta, comparison with experiment. The experimental values are taken from Hanson & Whitty (2014) and Padmanabhan et al. (2014).

2025). The 18% error of the full CO₂-He computation is difficult to understand at this level, and may reflect numerical non-convergence of elastic cross sections.

Fits—We fit all pressure broadening coefficients variation with the temperature spanning from 100 K to 800 K. Initially, we fit a linear power law (also known as Single Power Law, henceforth SPL), parametrized as:

$$\gamma_{0,|m|}(T) = \gamma_{|m|}(T_0) \cdot \left(\frac{T_0}{T}\right)^n \quad (15)$$

where $\gamma_{|m|}(T_0)$ denotes the pressure broadening at the standard reference temperature of 296 K. However, to capture the behavior of pressure broadening over a wide range of temperature to the requirement of the precision of 10% (Niraula et al. 2023), a Double Power Law (henceforth, DPL) is often required, as was discussed in the Stolarczyk et al. (2020) and as can be seen in Figure 5. We use the same formulation as Eq. 12 from Stolarczyk et al. (2020):

$$\gamma_{2,|m|}(T) = g_2 \cdot \left(\frac{T_0}{T}\right)^k + g'_2 \cdot \left(\frac{T_0}{T}\right)^{k'}, \quad (16)$$

which has four independent parameters (g_2 , j , g'_2 & j') which are listed in Table 3. In order to break the degeneracy that exists between g_2 , j , g'_2 , j' , while fitting the parameters, we enforce that g_2 is within 30% of the reference broadening parameter ($\gamma(T_0)$) obtained for the SPL. The DPL offers a better fit to our calculated pressure broadening parameters compared to SPL, although

the latter might be enough for JWST-related applications (see Figure 5). In the case of He, the power coefficients vary smoothly between the two computational approaches, while for H₂ a marked change is observed when moving from the RPA to the full-form treatment (see Figure 4). The underlying cause of this difference remains to be clarified and will be explored further in a subsequent study. As for the $|m|$ dependence, we model it with Padé approximation, defined as :

$$\gamma_x(|m|) = \frac{\sum_{i=0}^k a_i |m|^i}{1 + \sum_{j=1}^{k+1} b_j |m|^j} \quad (17)$$

where, a_0 takes the value of $\gamma_{m=0}$. It is common to use third order (i.e. $k=3$) for fitting this relation (e.g. Tan et al. 2022), for our purpose, we use a second order fit. We fit the above expression to the values in the Table 4 and the fits are shown in Figure 6. These fits enable extrapolation to values beyond the calculated range ($m > 50$) while smoothing out any irregular features.

The full table of pressure broadening coefficients is given in the Supplementary data; see a description in Appendix D, and is available via Zenodo¹.

¹ <https://zenodo.org/records/17161891>

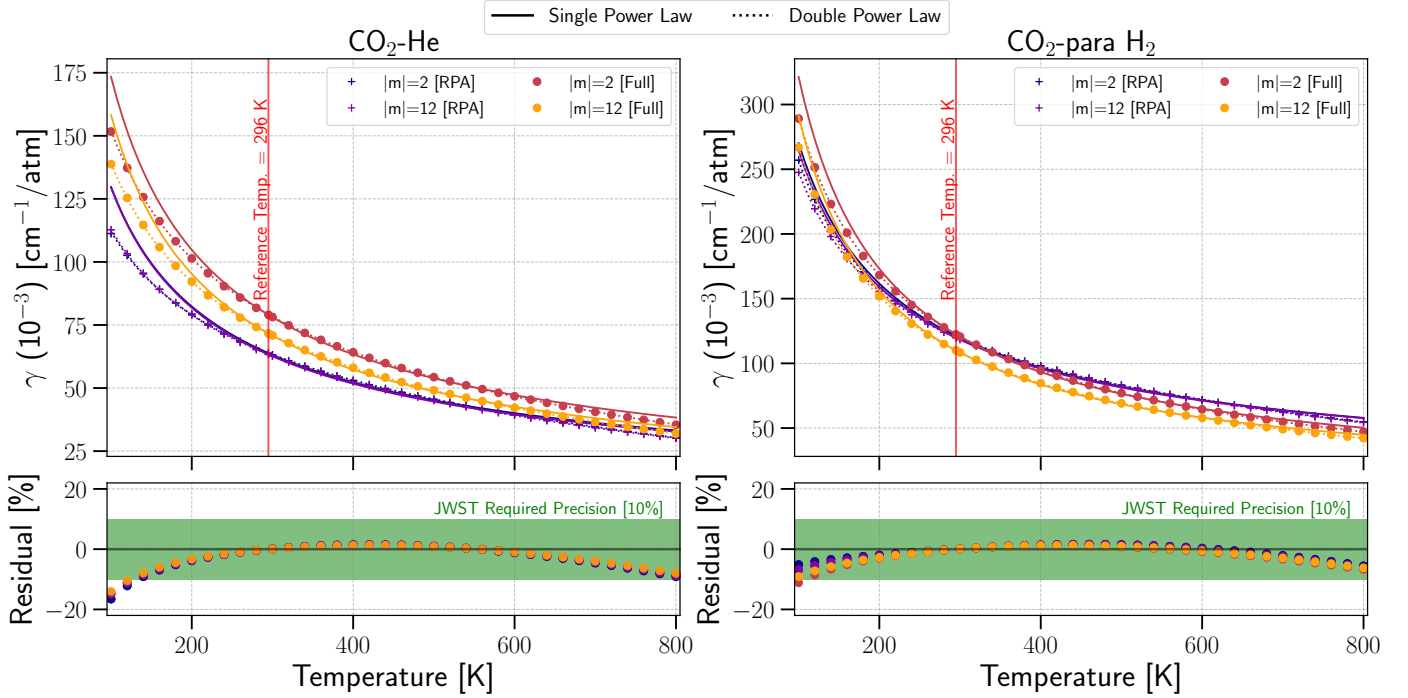


Figure 5. Broadening of CO₂-He as a function of temperature for two transitions ($m=2,12$) from two different methods for calculations and their corresponding fit in Single Power Law and Double Power Law. At both the low and high temperatures, SPL, plotted in solid line, tends to show large relative residuals ($>10\%$), while DPL, plotted in dotted line, yields a sub-percent precise fit. Residuals, which show the relative difference between the fit values vs the calculated values, are only shown for the SPL for clarity.

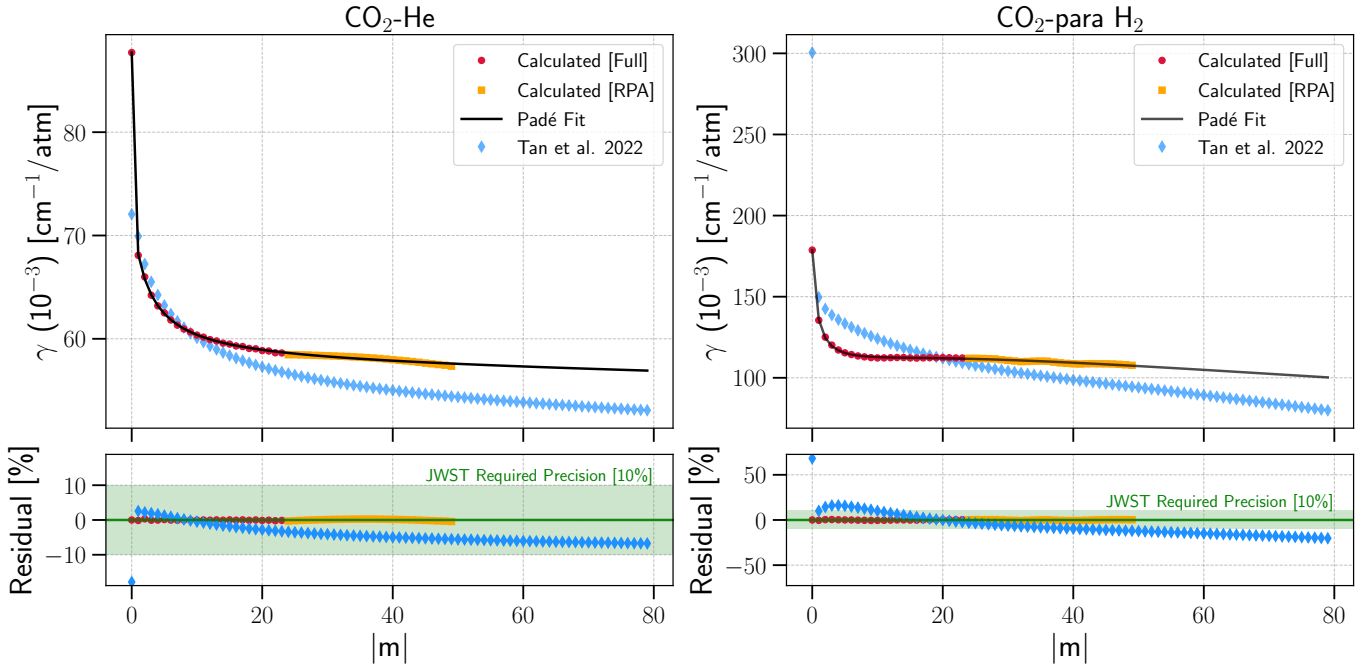


Figure 6. Fitting of Padé approximation to our computed pressure broadening values at the reference temperature (296 K). We fitted a second-order Padé approximation both for the broadening of helium and hydrogen, which are tabulated in Table 4. The residuals shown in both bottom panels are the relative difference between the Padé fit we obtained vs our calculated values and those suggested in Tan et al. (2022) (and used in HITRAN2020).

Table 3. Pressure broadening coefficients γ at 296 K for CO₂-He collisions and CO₂-H₂ γ is in 10^{-3} cm⁻¹/atm; m defined as in Appendix A; n as in Eq. (15); k, k', g_2, g'_2 from Eq. (16).

CO ₂ -He collision								CO ₂ -H ₂ collision							
Type	$ m $	$\gamma(T_0)$	n	g_2	k	g'_2	k'	Type	$ m $	$\gamma(T_0)$	n	g_2	k	g'_2	k'
Full	0	87.71	0.7387	93.38	0.5858	-5.518	-0.8578	Full	0	178.73	0.3986	182.95	0.2790	-4.726	-1.7478
Full	1	68.08	0.7077	72.40	0.5485	-4.221	-0.9403	Full	1	135.48	0.3934	139.13	0.2754	-3.854	-1.6724
Full	2	65.99	0.7260	74.83	0.5237	-8.698	-0.5256	Full	2	125.06	0.3922	128.81	0.2746	-3.810	-1.6086
Full	3	64.22	0.7315	72.76	0.5314	-8.400	-0.5167	Full	3	120.17	0.3897	123.90	0.2728	-3.750	-1.5840
Full	4	63.19	0.7337	72.50	0.5267	-9.162	-0.4685	Full	4	117.14	0.3869	120.55	0.2709	-3.451	-1.6353
Full	5	62.51	0.7364	71.26	0.5349	-8.599	-0.4809	Full	5	115.39	0.3872	118.92	0.2710	-3.550	-1.5941
Full	6	61.82	0.7359	69.98	0.5380	-8.015	-0.5099	Full	6	114.35	0.3894	117.93	0.2749	-3.551	-1.5702
Full	7	61.32	0.7353	69.07	0.5402	-7.606	-0.5311	Full	7	113.47	0.3901	116.70	0.2795	-3.195	-1.6305
Full	8	60.95	0.7353	68.59	0.5410	-7.496	-0.5331	Full	8	112.90	0.3901	116.40	0.2763	-3.458	-1.5770
Full	9	60.67	0.7358	68.28	0.5425	-7.469	-0.5284	Full	9	112.44	0.3907	115.97	0.2762	-3.500	-1.5668
Full	10	60.36	0.7350	67.80	0.5418	-7.295	-0.5422	Full	10	112.25	0.3924	115.49	0.2814	-3.206	-1.6182
Full	11	60.16	0.7351	67.44	0.5436	-7.134	-0.5488	Full	11	112.28	0.3964	114.90	0.2938	-2.596	-1.7416
Full	12	59.92	0.7338	67.56	0.5382	-7.502	-0.5276	Full	12	112.38	0.3998	114.59	0.3028	-2.217	-1.8391
Full	13	59.79	0.7344	66.98	0.5432	-7.046	-0.5536	Full	13	112.52	0.4042	114.14	0.3168	-1.632	-2.0436
Full	14	59.58	0.7332	67.16	0.5378	-7.436	-0.5300	Full	14	112.48	0.4059	113.89	0.3221	-1.435	-2.1305
Full	15	59.49	0.7339	66.69	0.5425	-7.059	-0.5488	Full	15	112.22	0.4056	113.67	0.3212	-1.466	-2.1151
Full	16	59.31	0.7328	66.73	0.5385	-7.278	-0.5375	Full	16	112.15	0.4055	113.68	0.3196	-1.549	-2.0741
Full	17	59.25	0.7336	66.29	0.5432	-6.895	-0.5598	Full	17	112.28	0.4087	113.65	0.3266	-1.383	-2.1436
Full	18	59.07	0.7321	66.43	0.5380	-7.223	-0.5409	Full	18	112.40	0.4108	113.65	0.3313	-1.258	-2.2079
Full	19	59.03	0.7328	66.39	0.5395	-7.221	-0.5357	Full	19	112.42	0.4128	113.57	0.3360	-1.154	-2.2624
Full	20	58.86	0.7313	66.33	0.5357	-7.325	-0.5350	Full	20	112.39	0.4128	113.62	0.3346	-1.234	-2.2107
Full	21	58.82	0.7319	66.17	0.5379	-7.209	-0.5386	Full	21	112.34	0.4144	113.52	0.3379	-1.173	-2.2405
Full	22	58.65	0.7304	66.14	0.5344	-7.343	-0.5333	Full	22	112.24	0.4137	113.44	0.3363	-1.202	-2.2256
Full	23	58.63	0.7311	66.03	0.5363	-7.268	-0.5348	Full	23	112.20	0.4154	113.29	0.3401	-1.101	-2.2852
Full	24	58.46	0.7293	66.30	0.5297	-7.703	-0.5118	Full	24	112.00	0.4132	113.30	0.3339	-1.292	-2.1729
RPA	25	58.46	0.6633	62.39	0.4949	-3.836	-0.9898	RPA	25	112.00	0.7063	112.54	0.6329	-0.599	-2.6289
RPA	26	58.44	0.6634	62.24	0.4971	-3.704	-1.0075	RPA	26	111.90	0.7061	112.33	0.6345	-0.539	-2.7157
RPA	27	58.43	0.6637	62.09	0.4992	-3.574	-1.0274	RPA	27	111.75	0.7057	112.13	0.6359	-0.483	-2.8086
RPA	28	58.40	0.6637	61.99	0.5003	-3.502	-1.0393	RPA	28	111.63	0.7048	111.86	0.6329	-0.505	-2.7711
RPA	29	58.38	0.6638	61.92	0.5014	-3.454	-1.0455	RPA	29	111.15	0.7004	111.51	0.6246	-0.608	-2.6294
RPA	30	58.36	0.664	61.79	0.5031	-3.349	-1.0638	RPA	30	110.72	0.6964	111.28	0.6167	-0.740	-2.4751
RPA	31	58.34	0.6641	61.67	0.5047	-3.261	-1.0782	RPA	31	110.38	0.6932	111.01	0.6099	-0.845	-2.3761
RPA	32	58.31	0.6641	61.69	0.5042	-3.290	-1.0724	RPA	32	109.96	0.6912	110.76	0.6120	-0.752	-2.4698
RPA	33	58.28	0.6639	61.65	0.5043	-3.286	-1.0723	RPA	33	110.08	0.6944	110.65	0.6232	-0.512	-2.7766
RPA	34	58.25	0.6638	61.63	0.5040	-3.299	-1.0708	RPA	34	110.28	0.6978	110.61	0.6317	-0.378	-3.0195
RPA	35	58.22	0.6638	61.56	0.5043	-3.274	-1.0731	RPA	35	110.32	0.6995	110.51	0.6367	-0.302	-3.2024
RPA	36	58.18	0.6636	61.60	0.5029	-3.349	-1.0592	RPA	36	110.26	0.6986	110.22	0.6333	-0.315	-3.1725
RPA	37	58.14	0.6633	61.59	0.5021	-3.375	-1.0556	RPA	37	109.71	0.6936	109.79	0.6241	-0.399	-2.9843
RPA	38	58.09	0.6629	61.59	0.5007	-3.421	-1.0494	RPA	38	109.21	0.6899	109.46	0.6178	-0.468	-2.8569
RPA	39	58.04	0.6625	61.67	0.4983	-3.561	-1.0235	RPA	39	108.91	0.6878	109.22	0.6144	-0.502	-2.8013
RPA	40	57.98	0.662	61.65	0.4967	-3.598	-1.0210	RPA	40	108.64	0.6863	109.01	0.6135	-0.497	-2.8093
RPA	41	57.92	0.6614	61.79	0.4933	-3.795	-0.9894	RPA	41	108.50	0.6870	108.89	0.6195	-0.389	-3.0083
RPA	42	57.86	0.6607	61.83	0.4908	-3.897	-0.9755	RPA	42	108.62	0.6905	108.84	0.6299	-0.256	-3.3517
RPA	43	57.80	0.6599	61.90	0.4877	-4.031	-0.9590	RPA	43	108.71	0.6929	108.78	0.6353	-0.201	-3.5561
RPA	44	57.73	0.6591	61.94	0.4848	-4.142	-0.9466	RPA	44	108.63	0.6932	108.73	0.6363	-0.195	-3.5779
RPA	45	57.65	0.6582	62.07	0.4808	-4.345	-0.9213	RPA	45	108.61	0.6940	108.67	0.6377	-0.184	-3.6294
RPA	46	57.58	0.6574	62.28	0.4764	-4.618	-0.8886	RPA	46	108.53	0.6944	108.50	0.6388	-0.169	-3.6963
RPA	47	57.51	0.6567	62.37	0.4734	-4.769	-0.8726	RPA	47	108.31	0.6942	108.24	0.6398	-0.152	-3.7891
RPA	48	57.45	0.656	62.43	0.4702	-4.909	-0.8600	RPA	48	108.03	0.6940	107.93	0.6413	-0.130	-3.9205
RPA	49	57.35	0.6525	62.27	0.4570	-5.050	-0.8754	RPA	49	107.72	0.6934	107.66	0.6426	-0.114	-4.0345
RPA	50	56.90	0.6425	60.55	0.4498	-3.865	-1.0920	RPA	50	107.52	0.6929	107.54	0.6433	-0.110	-4.0611

Table 4. Padé Approximations shown in Figure 6.

Parameter	CO ₂ -He		CO ₂ -H ₂	
	Tan et al. (2022)	This Work	Tan et al. (2022)	This Work
a_0	7.2060×10^{-2}	8.7710×10^{-2}	3.0051×10^{-1}	1.7868×10^{-1}
a_1	-2.2690×10^{-2}	4.8222×10^4	1.9992	1.3556×10^{-1}
a_2	1.0172×10^{-1}	1.5600×10^4	-2.8360×10^{-2}	5.4737×10^{-3}
a_3	1.1680×10^{-2}	...	6.3494×10^{-4}	...
b_1	-3.2460×10^{-1}	6.6505×10^5	1.4150×10^1	1.3080
b_2	1.4333	2.7100×10^5	2.7310×10^{-2}	4.2101×10^{-2}
b_3	2.1907×10^{-1}	6.7949×10^1	-9.2860×10^{-5}	1.6691×10^{-4}
b_4	8.9402×10^{-5}	...	6.2540×10^{-5}	...

6. COMPARISON TO EXPERIMENTAL VALUES AND HITRAN.

After scaling to the available measurements, our calculations closely followed the observed dependence on m (see Figure 4). For CO₂-H₂: the Hanson & Whitty (2014) measurement targeted P(24) transition of the 20012-00001 band at different temperatures, whereas Padmanabhan et al. (2014) covers P(16)-P(34) transitions of the 30012-00001 band at room temperature. (Spectroscopic notations, see Appendix A). Since very few transitions were available for CO₂-H₂ broadening in HITRAN, the air-broadening values (which are very comprehensive thanks to numerous studies, see Hashemi et al. (2020)) were scaled based on a factor obtained for P(24) transition values reported by Hanson & Whitty (2014). The constant value of the temperature dependence reported in the same value for all transitions was taken for *all* transitions of carbon dioxide in HITRAN. As shown in the Figure 6, it is clear that the rotational dependence of broadening due to air is appreciably different than that due to hydrogen, although in general, the aforementioned scaling (Tan et al. 2022) used in HITRAN was justified considering the lack of data at the time. As for the temperature dependence, the use of a constant value for all transitions, as expected, produces more controversial results as shown in Figure 7 where the prediction of low- m value is very different from our calculation.

For CO₂-He (which has been quite extensively studied): the broadening coefficients (γ_{He}) for the 30013-00001 band of CO₂ in the 1.6 μm region were investigated with continuous-wave cavity ring-down spectroscopy (Nakamichi et al. 2006) and the fit to these

data is used in the HITRAN2020 database (Gordon et al. 2022). Following the addition of this model to HITRAN2020 for the γ_{He} half-widths of CO₂, new measurements became available (Chen et al. 2021; Hendaoui et al. 2025) for the ν_3 band of CO₂, covering a much larger range of rotational quanta. In general, as can be seen from Fig. 6, the agreement with our calculations is better than for hydrogen, largely thanks to a larger amount of data available for He at the time when these parameters were estimated for HITRAN (Tan et al. 2022). The results from previous *ab initio* calculations from Korona et al. (2001) are at different temperatures, but they also agree well with our calculations (which provide broader rotational coverage).

The temperature dependence for CO₂-He was studied experimentally in Nakamichi et al. (2006); Deng et al. (2009); Brimacombe & Reid (1983). As explained in Tan et al. (2022) for HITRAN, the data from the latter two references were fitted to a linear function up to $m = 20$, while the value from Nakamichi et al. (2006) was omitted due to its very large difference with other measurements and calculations. A constant value of 0.58 was used for $|m|$ values larger than 20. With our complete set of calculations, we have a more precise estimate of this dependence. While at the reference temperature, the pressure broadening parameters are almost within the required 10%-precision for JWST data, as shown in Figure 6, the largest improvement on the pressure broadening parameters comes from the temperature dependence of the pressure broadening (see Figure 7).

As discussed here and in Hendaoui et al. (2025), for the CO₂-He, experimental values do not agree with one another, mainly because of the way to extract pressure broadening parameters from the lineshape analysis, (e.g. Deng et al. 2009). Given the close agreement with the recent experimental measurements, a $\pm 10\%$ error bar

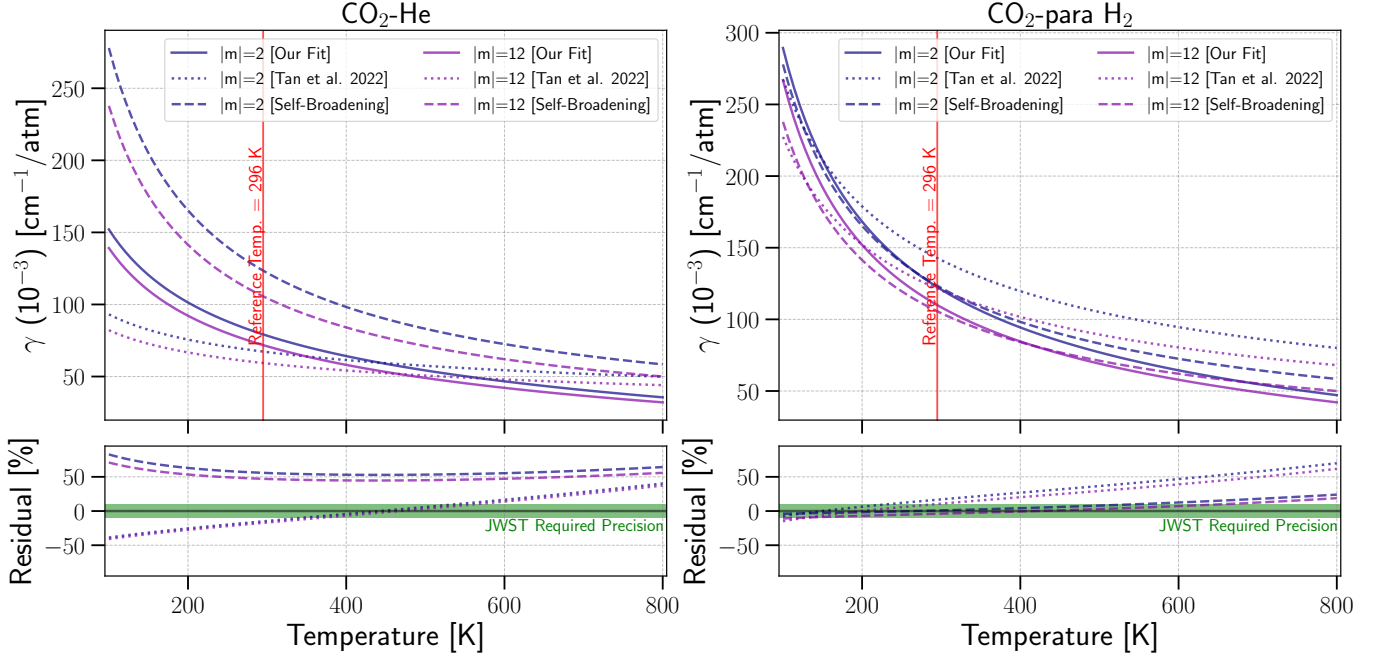


Figure 7. Comparison of the pressure broadening coefficients for two transitions ($m=2,12$) across 100 K to 800 K in comparison to previous state-of-the-art estimations. By refining the relevant power coefficients, we achieve the required improvements in the accuracy of pressure broadening coefficients to power instrument-limited exoplanetary studies in the *JWST* era. This contrasts with the parameters available before the present calculations, which were up to $5\times$ beyond the precision requirement away from our results (typically for $T \gtrsim 400$ K).

on our values is rather a conservative estimate of the uncertainty.

As shown in Figure 7, YUMI ultimately yields the collisional parameters targeting the 10% precision requirement for exoplanetary sciences with *JWST*. Our calculations allow estimating the collisional properties for a wide range of m and temperature spanning the parameter of interest for exoplanets, marking almost $5\times$ improvement compared to what was previously available.

7. CONCLUSION

We have computed the pressure broadening γ coefficients and the inelastic/elastic rates for the collision of CO_2 with He, para- H_2 . Both their dependence on the IR spectra line (the $|m|$ index) and their temperature dependence, from ~ 100 K up to ~ 800 K have been presented. The calculated and scaled collisional parameters are within the 10% precision requirement for exoplanetary sciences with *JWST* paving path to perform instrument-limited science in the *JWST* era, representing a significant improvement $5\times$ beyond the precision requirement away from experimental values at 296 K and our scaled values (typically for $T > 400$ K), and thus indeed inadequate Fits with parametrization comparable to HITRAN were made. The extension towards really high temperatures and high j_1 values ($j_1 \lesssim 250$)

is not realistic within an *ab initio* scheme. The role of the scheme presented here is to provide an anchor for the much more approximate methods to be used at $T \gg 800$ K, typical for HITEMP (Hargreaves et al. 2025).

While computing inelastic processes *ab initio* have been around for several decades now, in the realm of ISM conditions, the case here is much more difficult, because both of the temperature and the j_1 ranges, more akin to warm than to cold gases. We could demonstrate a convergence within less than 10% for the RPA computations (Figure 2). The absolute scale for the full computation is still not fully understood, and is probably sensitive to the details of the numerical solution of the Schrödinger equation. The numbers depend on the elastic matrix element of the T or S matrices, which are notoriously difficult to converge, like their classical counterparts, and are acutely sensitive to details of the rotational bases and computational scheme.

It is worthwhile to recall that comparison of scattering data with experimental values (like in this work or Thibault et al. (2001), and in various state-to-state inelastic scattering data, like Bergeat et al. (2020); Yang et al. (2010)) is way more difficult than comparison with spectroscopic data (Tennyson et al. 2024), because of the unbound character of the eigenfunctions, yielding no

discrete eigenvalues. Usually, the computation of scattering data ultimately resorts to an arbitrary unit experimental measurement of molecular flux, which must be compared with a quantum (or classical) computation. While Pressure Broadening should not involve such a scaling parameter, the difficult convergence and the precision needed made the use of *one scaling parameter* needed, enough to set the whole range of temperatures and $|m|$ values.

We also show that for CO₂, the vibrational dependence of the γ coefficients is smaller than the precision of both experiment and theory. This is the consequence of the weak dependence of the CO₂ geometry on the vibrational state, contrary to many H-containing molecules, especially H₂O, which facilitates collisional properties dependent solely on m . Considering that the isotopic dependence is also expected to be on a sub-percent level (Mondelain et al. 2025), the calculations carried out here can be used for all twelve stable isotopologues of carbon dioxide in HITRAN. Of course, these results can also be used for HITEMP (Hargreaves et al. 2025), ExoMol (Tennyson et al. 2024), AI-3000K (Huang et al. 2023), CDSD (Kochanov & Perevalov 2025) or any other database that provides rotational quanta for the lines of CO₂.

Software: MOLPRO (Werner et al. 2015), YUMI (Nemmedine et al. in prep)

Zenodo repository: The full table of pressure broadening coefficients is given in the Supplementary data at the following Zenodo repository (<https://zenodo.org/records/17161891>).

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APPENDIX

A. NOTATIONS

The angular momenta involved in the collision process are labeled as follows: j_1 , CO₂ (target) angular momentum; j_2 , H₂ (projectile) angular momentum; ℓ , the orbital angular momentum of the projectile with respect to the target in the laboratory frame. All combine to yield J , the total angular momentum of the collision in the laboratory frame, a conserved quantum number. The coupling scheme of the angular momenta is as follows (not writing the magnetic quantum numbers because of overall rotational invariance): $|j_1 >, |j_2 >; |j_1 > \otimes |j_2 > \mapsto |j_{12} >; |j_{12} > \otimes |\ell > \mapsto |J >$. We characterize the IR transition by the (pseudo-) quantum number m , which is $m = -k$, for the $P(k)$ transition and $m = k$ for the $R(k)$ transition. There is no Q branch here.

The kinetic energy of the collision (sometimes called the collision energy) is denoted by E . The total energy is $\mathcal{E} = E + E_1 + E_2$, where E_1 and E_2 are the internal energies (rotations, vibrations, ...) of the target 1 and the projectile 2. Here, as discussed in section 4.1, we do not add the vibrational energies to the internal energies. E_1 and E_2 are rotational energies only. The wavenumber associated with the collision is $k = \sqrt{2\mu E}/\hbar$, μ , reduced mass of the collision.

B. DETAILS OF PES COMPUTATION

B.1. Geometries

The geometry of the CO₂-H₂ colliding systems is presented in Figure B1. It follows the conventions of Green (1975), which is *not* identical to the rotator-target collisions conventions used in Valiron et al. (2008).

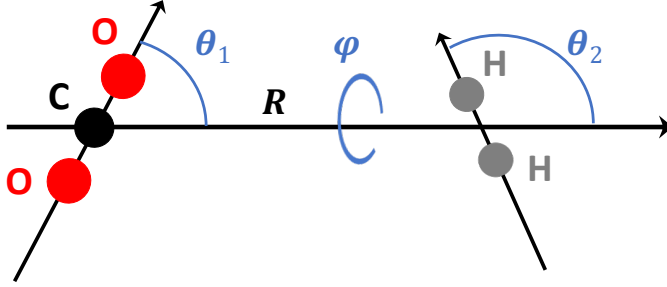


Figure B1. Geometry of the CO₂-H₂ complex.

B.2. Extrapolation to complete basis set

The basis sets used were the aug-CC-pVXZ type, from the MOLPRO basis set repository. We took $X = 3(T), 4(Q), 5$, and 6 basis sets (Pritchard et al. 2019). The extrapolation to the complete basis set was performed on the correlation energies, thanks to the formula:

$$E_{\text{CBS}} = \frac{E_X^X - E_{X-1}^{X-1}}{X^X - (X-1)^{X-1}} \quad (\text{B1})$$

with $X = 4, 5$. The Hartree-Fock contribution depends very weakly on the X values, we used the highest X available. We did use the aug-CC-pV6Z basis only to verify our extrapolation. All the results were in agreement to better than 0.5 cm^{-1} in the well region.

B.3. Fitting functions and coefficients for potential

We fit the PES's using the standard least square minimization (see Equation 13 and Wiesenfeld et al. (2025)).

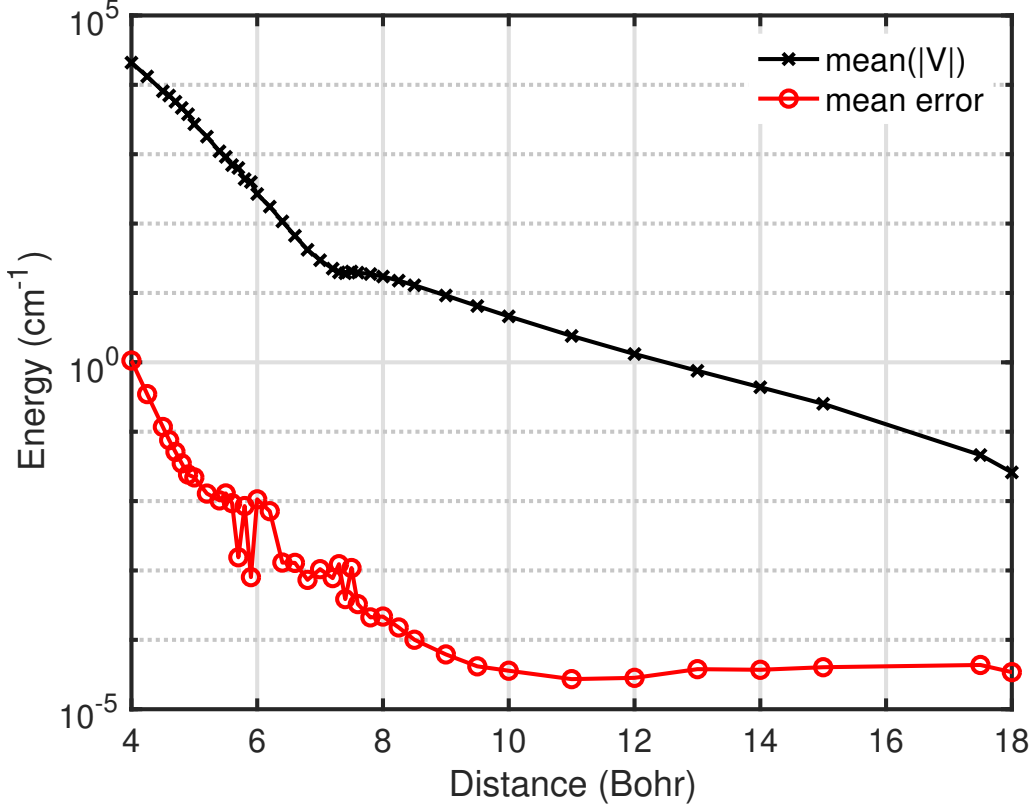


Figure B2. Quality of the fit for the $V_{\text{He-CO}_2}$ PES. Shown is the average of $|V(r, \theta)|$ over the angle θ and the average over θ error, $\epsilon = |V_{\text{fit}} - V_{\text{ab initio}}|/|V_{\text{ab initio}}|$.

C. DYNAMICS

C.1. Convergence of the dynamics

The integrator used in the dynamics (Manolopoulos 1986) requires three main parameters, namely, the initial point (RI), the final point (RF), and the step (STEP) (the version used was not with variable step). We kept RI within the inner forbidden region ($RI < 4$), RF well into the weak coupling region ($RF \geq 50$) - distances in bohr. $STEP$ is given as a fraction of the de Broglie wavelength at a large distance. The standard settings are $STEP=10$ for high energies and $STEP=50$ for low energies (here, $E \leq 0$ wavenumbers). The rotational basis set of CO_2 is taken such as at least 3 levels are closed, with energies $|E - E_{j_1}| > V_{\text{min}}$, where $|V_{\text{min}}|$ is the minimum value of the potential, taken at 250 and 60 cm^{-1} for H_2 and He targets, respectively.

The para- H_2 modification was limited to $j_2 = 0$ and the ortho- H_2 to $j_2 = 1$. We tried some computations with $j_2 = 0, 2$ but they proved intractable at $E > 200$, $j_1 \gtrsim 20$ because of the length of the computation and the size of the T matrix and the subsequent pressure broadening computation.

The next convergence parameter is the maximum value of the total angular J . While the convergence of the ordinary cross section Equation 7 is easy to test and achieve, the convergence of the pressure broadening is not (and all the

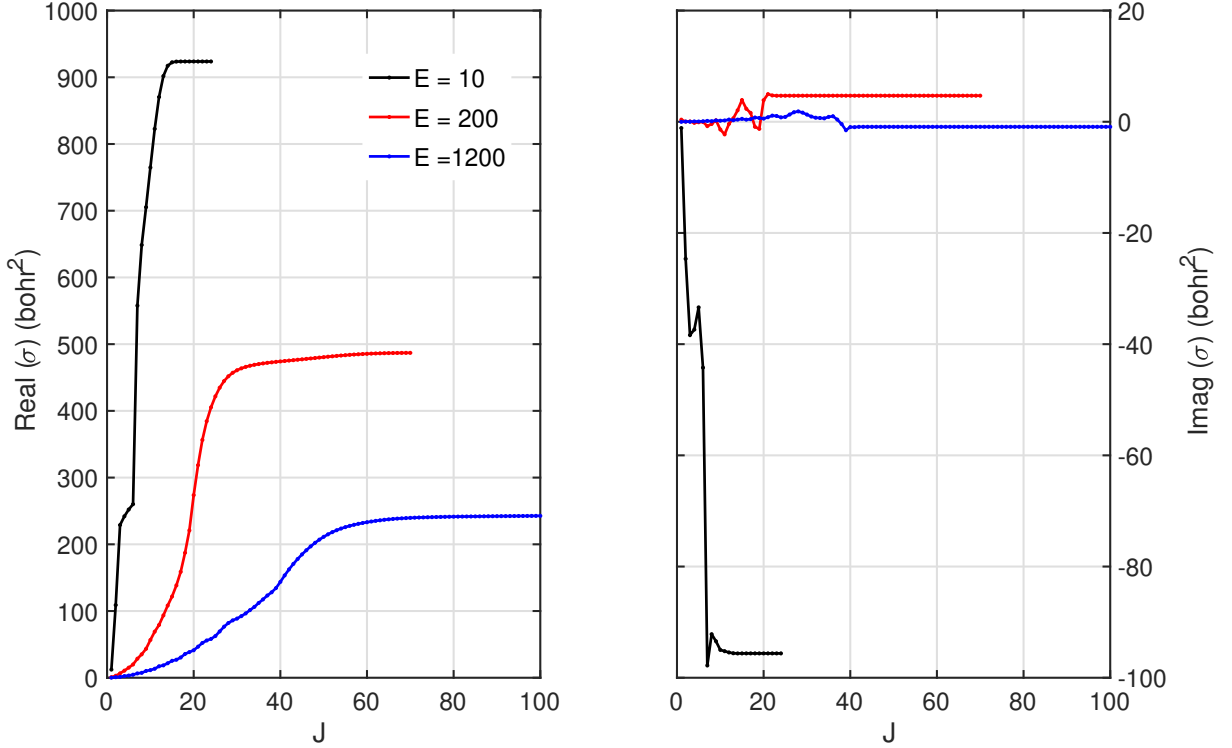


Figure C3. Convergence of the pressure broadening cross section for the CO₂–para H₂ and CO₂–He collisions, kinetic energies as shown. $m = -25$ transition. The cumulative sum of Eq. 1 plotted against the total angular momentum (J).

more for the pressure shift). Figure C3 shows the convergence obtained for representative cases, with collisions with He and H₂:

C.2. Convention for the rotator eigenfunctions: Normalization of Legendre polynomials and Legendre associated functions

Depending on the authors, several normalizations of Legendre polynomials and associated functions have been used. Thus, we clarify the normalization scheme used in our framework.

Knowing that the spherical harmonics obey the following normalization equation (stemming from the definition of rotor eigenfunctions) :

$$\int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} Y_{\ell m}^*(\theta, \phi) Y_{\ell' m'}(\theta, \phi) \sin \theta d\theta d\phi = \delta_{\ell \ell'} \delta_{m m'}, \quad (\text{C2})$$

The following normalizations and phases have been used. Note that existing scattering software and special function software may use different incompatible normalizations or phase conventions, but final observables should, evidently, be equal. We follow closely the MOLSCAT conventions, (Zare 1988, ch 1.3),

We have the following definition in

$$Y_{\ell m}(\theta, \phi) = \mathcal{P}_{\ell}^m(\theta) \Phi_m(\phi) \quad (\text{C3})$$

The normalizations are

$$\int_0^{2\pi} \Phi_m^*(\phi) \Phi_{m'}(\phi) d\phi = \delta_{m m'} \quad (\text{C4})$$

and

$$\int_0^{\pi} \mathcal{P}_{\ell}^{*m}(\theta) \mathcal{P}_{\ell'}^m(\theta) \sin \theta d\theta = \delta_{\ell \ell'} \quad . \quad (\text{C5})$$

Keeping in mind Equation C2, we have the following explicit forms:

$$\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}} \exp(im\phi) \quad (\text{C6})$$

and:

$$\mathcal{P}_\ell^m(\theta) = (-1)^m \left[\frac{2\ell+1}{2} \frac{(\ell-m)!}{(\ell+m)!} \right]^{1/2} P_\ell^m(\cos\theta) \quad (\text{C7})$$

where $P_\ell^m(\cos\theta)$ are associated Legendre functions, whose normalization is given by Eq. (C5) and Eq. (C7). The phase is chosen as:

$$\mathcal{P}_\ell^{-|m|}(\theta) = (-1)^m \mathcal{P}_\ell^{|m|}(\theta) \quad (\text{C8})$$

In the case $m = 0$, we find the usual reduction to Legendre polynomials:

$$\begin{aligned} Y_{\ell,0}(\theta, \phi) &= (2\pi)^{-1/2} \mathcal{P}_\ell^0(\theta) \\ &= \left(\frac{2\ell+1}{4\pi} \right)^{1/2} P_\ell(\cos\theta) \end{aligned} \quad (\text{C9})$$

These definitions are used in the normalizations and fit formulas of the YUMI code.

C.3. Normalization of cross sections

The normalization of the cross-sections/rates is a delicate matter, since it hinges on the chosen normalization of the associated Lagrange polynomials as well as those of the 6-j Wigner coefficients with respect to the 3-j and Clebsch-Gordon coefficients. Also, because of the statistical nature of the Pressure Broadening observable (Ben-Reuven 1966), one must be aware of the averaging/summing to be used for the quantum measurement. In our case, with the definition of all special functions and recoupling coefficients used, the normalization for PB sections reads:

$$N = \frac{1}{2j'_2 + 1} \sqrt{\frac{2j^< + 1}{2j^> + 1}} \quad , \quad (\text{C10})$$

with $j^>$ (resp. $j^<$) being the higher (resp. lower) value of the CO₂ rotational quantum number and j'_2 , the incoming projectile quantum number, if relevant (for He, it would be $j'_2 = 0$). Note that there is no factor associated with vibrational motion, for it has no degeneracy here. A more elaborate treatment is in order for all more involved cases (like symmetric/asymmetric/spherical rotors or degenerate vibrational modes).

D. TABLES

Full results are given in [Zenodo](#)², where a ReadMe contains the file descriptions. We also add the following for completeness:

Files 1: The coefficients of the $V(\text{CO}_2\text{--H}_2)$ PES, in the following format:

Line 1 : n

Line 2 : the n radial distances $r_1, \dots, r_n$

Following lines : $\ell_1 m_1 \ell_2 \ell$, {the n coefficients , one for each distance given in line 2 }.

Files 2: The coefficients of the $V(\text{CO}_2\text{--He})$ PES, in the same format, with $\ell_2 \equiv 0$ and $\ell = \ell_1$.

File 3 & 4: The pressure broadening γ scaled values (in $10^{-3} \text{ cm}^{-1}/\text{atmosphere}$) for CO₂–He & CO₂–H₂.

File 5 & 6: The power coefficients of the pressure for single power law and for Double power law.

File 7 & 8: The elastic & inelastic collision rates of CO₂–He & CO₂–H₂.

² <https://zenodo.org/records/17161891>

E. SCALABILITY

The primary computational bottleneck in YUMI arises during the matrix inversion required to solve the time-independent Schrödinger’s equation. While the detailed implementation will be presented in a dedicated paper on YUMI (Nejmeddine et al., in prep), the code uses highly optimized inversion routines from the LAPACK library, built with the recursive algorithm prescribed in (Ingemarsson & Gustafsson 2015). We are able to obtain roughly a scaling factor of $\mathcal{O}(\mathcal{N}^2)$ (see Figure E4). At higher energies (corresponding to higher temperatures and/or higher coupling factors), more energy levels are accessible, which increases both matrix size and computational time. In the current setup, we have successfully computed collisional parameters up to 800 K, representing a substantial progress. Additionally, memory usage presents an important consideration. YUMI dynamically allocates the memory for all variables, the largest of which corresponds to the coupling matrix for the potential energy, reaching up to several gigabytes. While is tractable for the current CO₂-H₂/He system, future applications involving more complex systems will necessitate stronger consideration for memory management as well as computational load. To address these challenges, we are actively exploring GPU-accelerated algorithms and machine-learning surrogate models to predict pressure broadening parameters for effectively modeling more complex collisional systems.

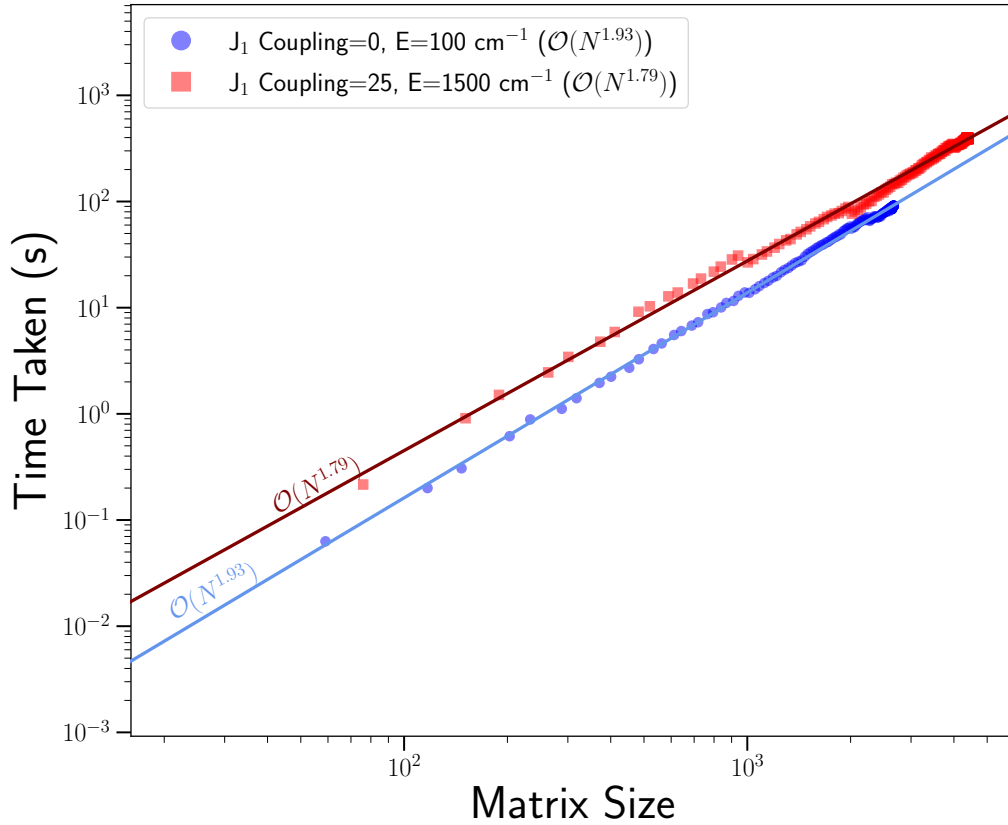


Figure E4. The time taken across different matrix sizes for two computational cases of CO₂-H₂ calculations at different J_1 -coupling and collisional energy. The calculation scales roughly at $\mathcal{O}(\mathcal{N}^2)$, with obvious discontinuities occurring near steps of 500, due to recursive matrix inversion which divides large matrices into sizes of 500 or smaller.

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