Collisional excitation of CO_2 by He :
Scattering calculations on a new potential energy surface

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Introduction

To evaluate CO_2 abudancy in astrophysical media, collisional data are needed. Hence, a new potential energy surface is computed for the CO_2-He van der Waals complex with a Coupled Clusters method and an extrapolation to the complete basis set. The surface is validated through the comparison of bound states and pressure broadening coefficients with experimental data. Finally, rate coefficients for the 5 - 300 K range of temperature and a study about CO_2 super-rotor in a helium-buffer-gas are provided.

Potential energy surface (PES)

- Computed with CCSD(T)/CBS(T,Q,5) method/basis set
- r(CO) = 2.1944 bohr

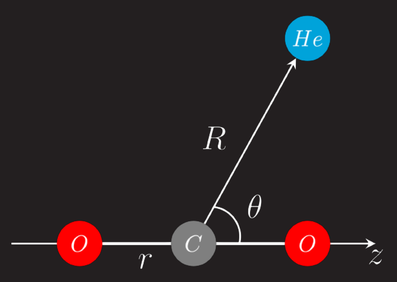


Figure 1: CO_2-He in Jacobi coordinates.

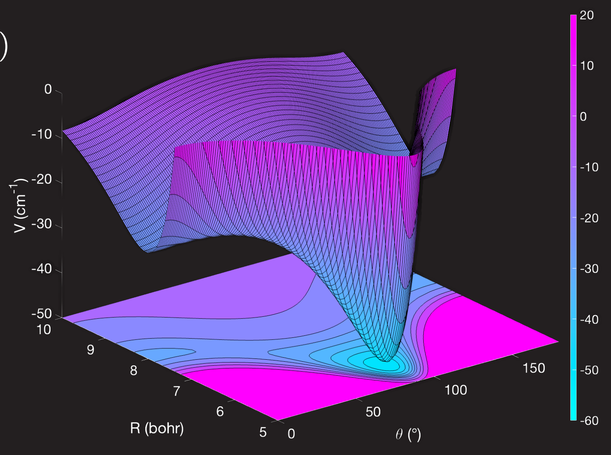


Figure 2: PES of the CO_2-He collisional system.

Reference	Global minimum		Local minimum	
	θ = 90°		θ = 0°	
	R (bohr)	V (cm^{-1})	R (bohr)	V (cm^{-1})
This work	5.78	- 49.22	8.05	- 26.51
Negri et al (1999)	5.86	- 45.98	8.13	- 26.31
Korona et al (2001)	5.81	- 50.38	8.03	- 28.94
Ran & Xie (2008)	5.79	- 49.39	8.06	- 26.70
Li & LeRoy (2008)	5.78	- 49.57	8.06	- 26.69

Table 1: Comparison between present and previous global and local minimas for the CO_2-He van der Waals complex.

Validation of the PES

Bound states:

- Close-Coupling (CC) approach with the BOUND program
- Frequencies of the $\Delta 0_{00}$ - 1_{01} **transition** within the ν_0 bound state

	Isotopes	This work	Korona et al [1]	Li & LeRoy [2]	Ran & Xie [3]
ν (cm^{-1})	$^{12}C^{16}O_2$	0.5885	0.592	0.5881	0.589
abs. error (%) [4]		0.522	0.072	0.583	0.436
ν (cm^{-1})	$^{13}C^{16}O_2$	0.5877		0.5873	
abs. error (%) [5]		0.530		0.590	

Table 2: Frenquencies and absolute error between our calculations and experimental measurements of the $\Delta 0_{00}$ - 1_{01} transition within the ν_0 bound state for $^{12}CO_2$ and $^{13}CO_2$ isotopes.

⇒ Validation of the **depth** and **shape** of the potential **well**

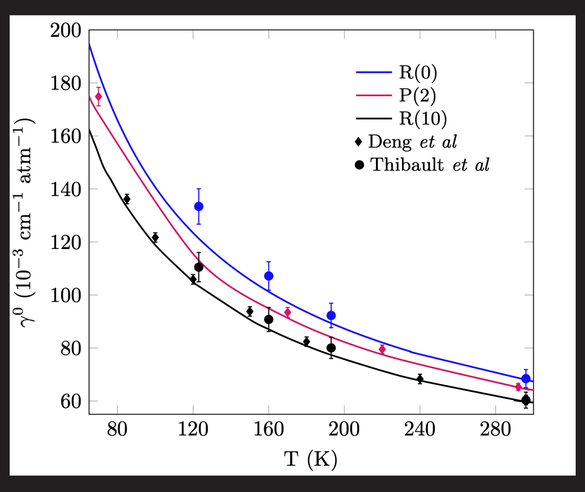
Pressure broadening:

- Lines Lorentzian shaped → half width at half maximum (HWHM) γ^0:

$$\gamma^0_{\chi\chi'} = n_p \nu \overline{\sigma_{\chi\chi'}} = \frac{56.6915}{\sqrt{\mu T}} \overline{\sigma_{\chi\chi'}}$$

χ, χ': rovibrational levels involved ; $\nu = (8k_BT/\pi\mu)^{1/2}$; n_p : density of perturbers

$\overline{\sigma_{\chi\chi'}}$: Maxwellian average of collisional cross section at a given temperature T.



- Full CC calculations with MOLSCAT
- Transitions between ν_0 and ν_3 vibrational states

Figure 3: HWHM for R(0) (blue), P(2) (magenta) and R(10) (black) in ν_3 from theroretical (line) and experimental studies of Deng *et al* [6] (♦) Thibault *et al* [7] (•).

⇒ Validation of the **repulsive** part of the PES

Results and discussions

CO_2 - He rate coefficients:

- Maxwellian average of **cross sections**
- Cross sections computed by a CC approach with MOLSCAT program

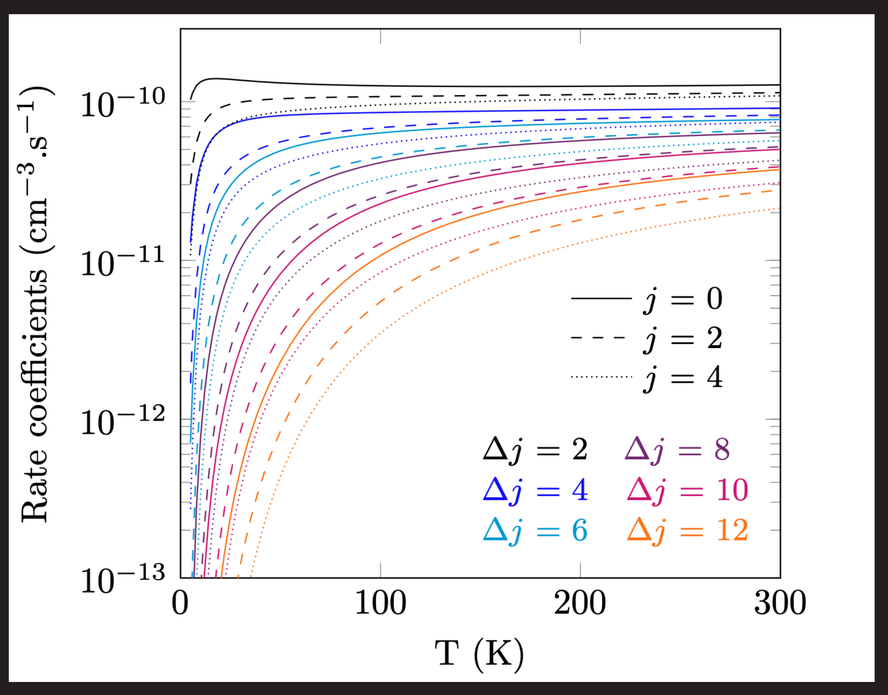


Figure 4: Excitation rate coefficients from j = 0, 2, 4 for various Δj as a function of temperature.

- At **fixed** Δ**j**, rate coefficients **increases with initial** j and reach an **asymptotic** value
- When Δ**j increases**, the quenching is **decreasing**

Stable CO_2 super-rotor:

- Stable CO_2 **rotationally highly excited** → potential system for inelastic transitions and cold chemistry studies
- Elastic process > rotational quenching at T_{cryo}(He) → **stable super-rotors**

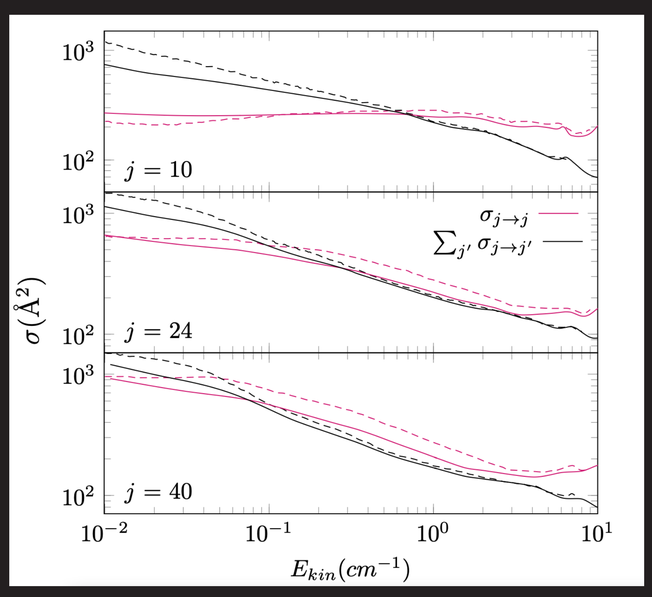


Figure 5: Elastic (magenta) and sum of inelastic (black) cross sections for CO_2 and He collision at j = 10, 24, 40 in alQady [8] *et al* (dashed) and our (plain) study.

- Our $\sigma_{j\to j}$ are **lower**
- Our crossing energies are **higher** $\forall$ j

} Stability **overestimated**

- $\Delta V_{glob.min.}$ (PESs) < **1%** → **up to 30%** difference on quenching rates

⇒ At **low energy**, cross sections are **really sensitive** to the PES

References

[1] T. Korona, R. Moszynski, F. Thibault, JM. Launay, B. Bussery-Honvault, P. Wormer, J. Chem. Phys. **115** (2001)
[2] H. Li & R. LeRoy, Phys. Chem. Chem. Phys. **28** (2008)
[3] H. Ran & D. Xie, J. Chem. Phys. **128** (2008)
[4] Y. Xu & W. Jäger, J. Mol. Struc. **599** (2001)
[5] A. R. W. McKellar, J. Chem. Phys. **11** (2008)
[6] W. Deng, D. Mondelain, F. Thibault, C. Camy-Peyret, A. W. Mantz, J. Mol. Spectrosc. **256** (2009)
[7] F. Thibault, B. Calil, J. Boissoles, JM. Launay, Phys. Chem. Chem. Phys. **2** (2000)
[8] W. H. al-Qady, R. C. Forrey, B. H. Yang, P. C. Stancil, N. Balakrishnan, Phys. Rev. A **84** (2011)