

SUPPORTING INFORMATION

Behavior and modelling of the vibrational-to-translational temperature ratio at long time scales in CO₂ vibrational kinetics.

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1. CO₂ Vibrational levels, energies and degeneracies

The following table lists the considered vibrational levels, specified by the quantum numbers $(i_1 i_2 i_3)$, their energies and degeneracies (g). The vibrational energies are computed from equation 2 of the paper and the degeneracies from $i_2 + 1$.

i_3	$E_{\text{vibrov}} (\text{eV})$ $E_{(i_1 i_2 i_3)}$			
	$i_1 = 0$	$i_2 = 1$	$i_2 = 2$	$i_2 = 3$
	$i_2 = 0$ ($g = 1$)	($g = 2$)	($g = 3$)	($g = 4$)
0	0.000	0.083	0.166	0.250
1	0.291	0.373	0.454	0.536
2	0.579	0.659	0.739	0.820
3	0.864	0.943	1.021	1.100
4	1.146	1.223	1.300	1.378
5	1.425	1.501	1.576	1.652
6	1.701	1.775	1.849	1.923
7	1.974	2.046	2.119	2.191
8	2.243	2.314	2.385	2.456
9	2.510	2.579	2.649	2.718
10	2.773	2.841	2.909	2.977
11	3.034	3.100	3.166	3.233
12	3.291	3.356	3.420	3.486
13	3.545	3.608	3.672	3.735
14	3.796	3.858	3.920	3.982
15	4.044	4.104	4.165	4.225
16	4.289	4.348	4.406	4.465
17	4.531	4.588	4.645	4.703
18	4.770	4.825	4.881	4.937
19	5.005	5.059	5.113	5.168
20	5.238	5.290	5.343	5.396
21	5.467			

The vibrational levels $((i_1 + 1) i_2 i_3)$ and $(i_1 (i_2 + 2) i_3)$ are coupled due to the proximity of their energy and therefore are grouped into a single species. The total degeneracy of the species is the sum of the degeneracies of the grouped states and is referred to as statistical weight. The following table summarizes the statistical weight of the vibrationally excited species based on the coupled symmetric sublevels.

Species	Grouped vibrational states ($i_1 i_2 i_3$)	Degeneracies of grouped states $g = i_2 + 1$	Statistical weight of species $\sum (i_2 + 1)$
CO ₂ v _a	(0 1 0)	2	2
CO ₂ v _b	(0 2 0), (1 0 0)	3, 1	4
CO ₂ v _c	(0 3 0), (1 1 0)	4, 2	6
CO ₂ v _n	(0 0 n)	1	1
CO ₂ v _{n,a}	(0 1 n)	2	2
CO ₂ v _{n,b}	(0 2 n), (1 0 n)	3, 1	4
CO ₂ v _{n,c}	(0 3 n), (1 1 n)	4, 2	6

2. COMSOL Multiphysics solver

The solution of the modelling equations for the different combination of parameters' values was achieved through a parametric sweep, varying one parameter at a time until all combinations were solved. A time-dependent study with a time limit of 0.03 s was used, meaning that for each parameter combination the simulation ran until 0.03 s. This time was proven to be enough to reach the steady state.

The chosen time stepping method was a Backwards Differentiation Formula with minimum order of 1 and a maximum order of 2. An initial time step of 10^{-18} s was used to ensure consistent initial conditions and, as the time-dependent solution progressed, a variable time step was employed.

The equations were solved in a logarithmic formulation, given the very small numbers expected for the dependent variables. An absolute tolerance of 0.001 was specified for all variables in their logarithmic form, which corresponds to a relative tolerance of approximately the same value for the variables in their non-logarithmic form.

The shared-memory multiprocessing parallel direct sparse solver, also known as the PARDISO solver, was the algorithm used to solve the fully coupled set of equations. Moreover, a constant Newton-Raphson method with a minimal Jacobian update was also specified to minimize the solution time.

Further information on the parametric sweep, the time-dependent study and the solver options and configurations can be found in the COMSOL Multiphysics Reference Manual.