# **Supplementary Information for Publication**

# Increase of Radiative Forcing through Mid-IR Absorption by Stable CO<sub>2</sub> Dimers?

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# Supplementary text, figures, and tables

### Thermodynamic stability of the (CO<sub>2</sub>)<sub>2</sub> dimer

Figure S1 shows that the free enthalpy of dimerization is steeply decreasing with temperature. At about 50 K, the dimerization becomes exergonic, which means that the monomer is thermodynamically favored. Above 50 K the equilibrium constant  $K = \exp\left(\frac{-\Delta G}{RT}\right)$  is > 1 (c.f. Figure 1), meaning that the monomer fraction in the gas's total composition must be higher than the dimer fraction. At very low temperatures (< 50 K) entropy favors the dimer. Above 50K the monomer starts to be the dominant species, and the equilibrium constant increases steeply. That said, we may not expect any significant number of (CO<sub>2</sub>)<sub>2</sub> dimers for conditions such as on Earth's surface (288K), on Mars (210K) or even on Venus (737K). However, it has been proven that dimers do exist on Venus <sup>S1</sup>. This is due to the pressure dependence of the monomer-dimer equilibrium.

The pressure dependent degree of dissociation for a given equilibrium constant  $K_{eq}(T)$  is:

$$\alpha(T,p) = \sqrt{\frac{K_{eq}(T)}{K_{eq}(T) + 4 * p/p_0}}$$

As one may see from Figure S2, the mixing ratio of carbon dioxide on Venus with 88.8 bars is high enough so that  $\alpha \approx 0.85$ . Hence, we can expect a significant amount of  $(CO_2)_2$  dimers on Venus, while for the other above-mentioned conditions, the mixing ratio is so low that  $\alpha \approx 1.0$ , meaning complete dissociation. We now may compute the dimer fraction  $x_a(T,p)$  or monomer fraction  $x_b(T,p)$ :

$$x_a(T,p) = \frac{1 - \alpha(T,p)}{1 + \alpha(T,p)}, \ x_b = \frac{2 \cdot \alpha}{1 + \alpha}.$$

Figure S2 shows the pressure dependency of the dimer fraction  $x_a(T,p)$  for the three equilibrium constants  $K_{eq}(T)$  we computed for Earth, Mars, and Venus. This allows us to estimate the actual dimer fraction  $x_a(T,p)$  for the specific carbon dioxide partial pressure on these planets. Finally, we can estimate the partial pressure of the dimer

$$p(dimer) = x_a(T,p) * p(CO_2)$$

and the dimer-monomer ration by

dimer – monomer ratio = 
$$\frac{x_c}{x_l}$$



**Figure S1. Thermochemistry of**  $(CO_2)_2 \leftrightarrow 2 * CO_2$  **dissociation.** Above temperatures of 50 K, the change of free enthalpy of dimerization  $\Delta G^0$  turns negative (left plot), mainly driven by the change of dimerization entropy  $T * \Delta S^0$ , which becomes increasingly positive with increasing temperature. Consequently, the dissociation of the dimer is favored above 50 K. The temperature dependence of the free enthalpy of dimerization  $\Delta G^0$  is not perfectly linear when going to very high temperatures (right plot).



Figure S2. Pressure dependence of the degree of dissociation  $\alpha(T,p)$  and dimer fraction  $x_a(T,p)$ . For partial pressures of carbon dioxide greater than 1 (= 10<sup>0</sup>) bar, the degree of dissociation  $\alpha(T,p)$  becomes significantly lower than 1, meaning that not all dimer is dissociating (left plot). Consequently, also the dimer fraction  $x_a(T,p)$  depends on the partial pressure of carbon dioxide (right plot). This allows for an estimation of the dimer fraction. For example, on Earth (yellow) the partial pressure of carbon dioxide is 4.20\*10<sup>-4</sup> bar, leading to a dimer fraction of 7.34\*10<sup>-7</sup> and consequently to a partial pressure of the carbon dioxide dimer of 3.1\*10<sup>-4</sup> µbar mentioned in Table 1.

### Anharmonic vibrational frequencies from the multi-mode PES based VSCF/VCI approach

In Figure 3, we employ scaling factors for both the frequencies and the intensities to better compare the computed data with the experimental data. On the one hand, these scaling factors are necessary to account for the frequency shifts introduced by the surrounding neon matrix, a purely physical phenomenon. On the other hand, these scaling factors also compensate for the small remaining anharmonicity deficit in our calculations, a purely numerical phenomenon. The latter is due to the multi-mode PES, which approximates the exact PES and allows for good results if converged. There are two major possibilities to converge the PES and improve the results: (1) Expand the multi-mode PES beyond 3-mode couplings. In theory, for (CO<sub>2</sub>)<sub>2</sub> there could be up to 12-mode couplings involved in the PES. (2) Use a better method than DCSD-F12/VDZ-F12 for computing the electronic structure. Both improvements regarding the computational approach, however, are costly in terms of computational resources. Thus, we decided to accept slight discrepancies between the VSCF/VCI computed anharmonic frequencies and the "real" gas-phase frequencies.

Table S1. Calculated CO2 monomer ( $D_{\infty h}$ ) vibrational frequencies and IR intensities in cm<sup>-1</sup>DCSD-F12/cc-pVDZ-F12 (used for assignment)

Mode	Label (Irrep)	Harmonic	VSCF	IR Intensity	VCI(SDTQ)	IR Intensity			
4	v <sub>3</sub> (A <sub>1u</sub> )	2399.04	2356.42	990.5	2351.03	1000.03			
3	$v_1(A_{1g}), 2 v_2(E_u)$	1364.13	1352.3	0	1295.55 / 1399.55	0			
	"fermi resonance"								
2	v <sub>2</sub> (E <sub>u</sub> )	677.09	674.15	57.73	673.13	57.76			
1	v <sub>2</sub> (E <sub>u</sub> )	677.08	674.15	57.73	673.13	57.76			

DCSD-F12/cc-pVDZ-F12 (used for assignment)							
Mode	Label (Irrep)	Harmonic	VSCF	IR Intensity	VCI(SDTQ)	IR Intensity	
12	$v_9(B_u)$	2400.64	2363.42	1913.88	2353.16	695.04	
11	$v_1(A_g)$	2395.68	2358.9	0	2346.99	0	
10	$v_2(A_g)$	1363.72	1350.06	0	1302.19	0.06	
9	v <sub>10</sub> (B <sub>u</sub> )	1363.71	1350.89	0.25	1305.68	0.15	
8	$v_7(A_u)$	679.65	684.85	109.89	677.04	106.77	
7	$v_3(A_g)$	676.46	686.16	0	671.24	0	
6	$v_6(B_g)$	675.79	681.37	0	673.6	0	
5	v <sub>11</sub> (B <sub>u</sub> )	674.14	683.91	138.59	669.16	131.62	
4	$v_4(A_g)$	104.02	115.03	0	98.93	0	
3	$v_5(A_g)$	45.32	50.84	0	42.9	0	
2	$v_8(A_u)$	27.58	67.42	0	45.46	0	
1	v <sub>12</sub> (B <sub>u</sub> )	26.35	81.67	0.19	49.72	0.19	
		DCSI	D-F12/aug-cc	-pVDZ			
Mode	Label (Irrep)	Harmonic	VSCF	IR Intensity	VCI(SDTQ)	IR Intensity	
12	$v_9(B_u)$	2401.68	2363.97	1897.84	2354.01	765.63	
11	v <sub>1</sub> (A <sub>g</sub> )	2396.69	2362.35	0.00	2352.23	0.00	
10	$v_2(A_g)$	1364.05	1350.59	0.23	1307.85	0.13	
9	v <sub>10</sub> (B <sub>u</sub> )	1363.99	1349.85	0.00	1303.90	0.00	
8	$v_7(A_u)$	682.79	687.20	109.54	679.39	107.02	
7	$v_3(A_g)$	679.99	688.45	0.00	673.63	0.00	
6	$v_6(B_g)$	679.24	683.67	0.00	675.86	0.00	
5	v <sub>11</sub> (B <sub>u</sub> )	677.33	685.70	139.98	671.01	133.81	
4	$v_4(A_g)$	105.07	114.79	0.00	98.43	0.00	
3	$v_5(A_g)$	45.26	50.03	0.00	42.74	0.00	
2	λ. (Λ <sup>-</sup> )	26.07	66 15	0.00	15 27	0.00	
	V <sub>8</sub> (A <sub>u</sub> )	20.97	00.15	0.00	45.57	0.00	





(left) The antisymmetric stretch region (left), containing the  $(CO_2)_2 v_9(B_u)$  transition and (right) the bending region, containing the  $(CO_2)_2 v_8(A_u)$  and  $v_{11}(B_u)$  transition. The calculated frequencies (colored lines) are not scaled, in contrast to Figure 3, which shows the same results including scaling factors.

## Results from matrix isolation infrared (MI-IR) spectroscopy of carbon dioxide in neon

### Numerical integration of the band areas in the Ne matrix spectra

In total, we evaluate 13 different mixing ratios of  $CO_2$ :Ne, being 1:10000 (100 ppm  $CO_2$ ), 1:5000 (200 ppm  $CO_2$ ), 1:3333 (300 ppm  $CO_2$ ), 1:2500 (400 ppm  $CO_2$ ), 1:2000 (500 ppm  $CO_2$ ), 1:1429 (700 ppm  $CO_2$ ), 1:1000 (1000 ppm  $CO_2$ ), 1:500 (2000 ppm  $CO_2$ ), 1:333 (3000 ppm  $CO_2$ ), 1:250 (4000 ppm  $CO_2$ ), 1:200 (5000 ppm  $CO_2$ ), 1:133 (7500 ppm  $CO_2$ ), 1:100 (10000 ppm  $CO_2$ ). The marker bands were integrated using carefully chosen integration limits. The colors in all subsequent figures correspond to the color scheme used in Figure 3, Table 3, Table S1, Table S2 and Figure S3. Figure S4 and Figure S5 summarize the integration limits, which are maintained for all carbon dioxide mixing ratios. Above 4000 ppm, the intensity in the stretching region (2350 cm<sup>-1</sup>) is too high for the detector, leading to unreasonable band-shapes. Thus, the stretching region was evaluated only up to 4000 ppm. We decided to include the evaluation at 3000 ppm and 4000 ppm, yet, this must be appreciated with care because also here we observe a band-splitting that may be due to the intensity overflow. Figure S4 depicts the integration for our main set of experiments, where the gas was mixed at 25°C, while Figure S5 comprises the second set of experiments, where the gas was mixed at 65°C.







**Figure S4.** MI-IR spectra of  $CO_2$ :Ne mixtures containing (a) 100 ppm to 500 ppm, (b) 700 ppm to 4000 ppm, and (c) 5000 ppm to 10000 ppm carbon dioxide. The mixtures were equilibrated at 25°C and isolated at 6.0 K. The IR spectra were recorded at 6 K, with a resolution of 0.3 cm<sup>-1</sup> using 512 scans.



**Figure S5.** MI-IR spectra of  $CO_2$ :Ne mixtures containing 200 ppm to 1000 ppm carbon dioxide. The mixtures were equilibrated at 65°C and isolated at 6.0 K. The IR spectra were recorded at 6 K, with a resolution of 0.3 cm<sup>-1</sup> using 32 scans.

#### Dimer contribution to the absorption cross-sections in the Ne matrix spectra

We here provide more details on the results of our numerical integration, specifically the evaluation of the dimer fraction  $x(CO_2)_2$  and the relative increase of band area  $\Delta A$  due to dimerization (c.f. Figure 4). We here elaborate on the absolute (Figure S6a) and relative (Figure S6b,c) areas of the individual marker bands by spectral regions. In the stretching region (Figure S6b, left) at 100 ppm carbon dioxide concentration, the  $CO_2 v_3(A_{1u})$  transition at 2348.3 cm<sup>-1</sup> amounts to 94.4% of the total band area, while the  $(CO_2)_2 v_9(B_u)$  transition at 2350.2 cm<sup>-1</sup> has 5.0%. In contrast, at 400 ppm, the monomer  $v_3(A_{1u})$ transition at 2348.3 cm<sup>-1</sup> has a contribution of 83.5% to the total area, while the dimer  $v_9(B_u)$  transition at 2350.2 cm<sup>-1</sup> has 15.0% (monomer-per-dimer ratio  $\frac{0.83}{0.15} = 5.5$ ). In other words, the contribution of the (CO<sub>2</sub>)<sub>2</sub> bands is 3 times higher at 400 ppm than at 100 ppm carbon dioxide mixing ratio. At 1000 ppm the dimer band contribution increases merely to 18.7%. Hence, the dimer's contribution increases steeply at low mixing ratios and only marginally at high ratios. In the bending region (Figure S6b, right) at 100 ppm, the CO<sub>2</sub> monomer v<sub>2</sub>(E<sub>1u</sub>) transition at 668.5 cm<sup>-1</sup> and 667.9 cm<sup>-1</sup> has a contribution of 97.4%, while the  $(CO_2)_2$  dimer  $v_8(A_u)$  transition at 670.3 cm<sup>-1</sup> has 1.0 % and the  $(CO_2)_2$  dimer  $v_{11}(B_u)$ transition at 664.6 cm<sup>-1</sup> has 1.7 %. At 400 ppm, the monomer contributes 87.0%, while the two dimer bands contribute 12.9% in sum (monomer-per-dimer ratio  $\frac{0.83}{0.15} = 6.7$ ). Consequently, the dimer bands' contribution is 4.5 times higher at 400 ppm than at 100 ppm. At 1000 ppm, the monomer and dimer bands amount to 78.4% and 21.6%, respectively. Consequently, the dimer bands' contribution is only 1.7 times higher at 1000 ppm than at 400 ppm carbon dioxide concentration. This observation confirms the picture seen in the stretching region. Figure S6b and S6c show the results for the gas mixing temperature of approximately 25°C and 65°C. The differences are most likely experimental discrepancies. Hence, we argue that within the chosen gas mixing temperature range of 25°C to 65°C there is no influence on the dimer fraction.



**Figure S6.** (a) Absolute and (b) relative area under the marker bands on a logarithmic ppm  $CO_2$  scale, regarding  $CO_2$ :Ne gas mixtures at 25°C. (c) Relative area under the marker bands regarding  $CO_2$ :Ne gas mixtures at 65°C.

#### Heating of CO<sub>2</sub> trapped in Ne matrices

We mixed carbon dioxide (200 ppm, 300 ppm, 400 ppm, 500 ppm and 1000 ppm) with neon and equilibrated the mixtures at 65°C. For this purpose, the whole mixing apparatus was heated continuously. Each of the matrices was deposited at 5.8 K and then heated to 100 K. Figure S7 shows how the spectra change due to heating for 500 ppm CO<sub>2</sub>. In the slow heating process from 5.8 K to 9.0 K the intensity ratio remains perfectly constant. This implies that the matrix is immobile, not allowing for cage-to-cage diffusion of CO<sub>2</sub> molecules. That is, CO<sub>2</sub> is indeed trapped – as desired for MI-IR experiments. At 9.5 K, the intensities start to decrease as a whole, implying sublimation of a significant fraction of neon, together with some CO<sub>2</sub>. At 10 K, we observe a broad band, which signifies that practically all neon has sublimed, whereas some of the less volatile CO<sub>2</sub> remains on the sample holder. The broad band indicates an amorphous solid state,  $(CO_2)_n$ , where larger and larger clusters eventually develop to the amorphous solid. The amorphous CO<sub>2</sub> then remains upon continued heating to at least 30 K, as indicated by the broad and featureless band in Figure S7 between 10.0 and 30.2 K. At 40 K. features start to develop in this band, indicating the crystallization of the amorphous solid, where the features develop up to 80 K. At even higher temperatures the vapor pressure of crystalline CO<sub>2</sub> becomes too high so that the solid sublimes and is pumped off. This experiment demonstrates that the matrix is immobile at 6 - 9 K so that the composition of the gas-phase is retained in the neon matrix.



**Figure S7.** Heating experiment. 500 ppm  $CO_2$  mixed with neon at 65°C and isolated at 6 K, then heated to the indicated temperatures.



**Figure S8**. MI-IR spectra of air deposited at 15 K for deposition times of 15 min, 30 min, 3h, 4h, 6h and 8 h. Assignment of the peaks is presented in Table S3, where the indicated molecules are assigned based on [a] ref. <sup>\$2</sup>, [b] ref. <sup>\$3</sup>, [c] ref. <sup>\$4</sup> and [d] ref. <sup>\$5</sup>.

Species	Wavenumber / cm <sup>-1</sup>	Reference / cm <sup>-1</sup>
H <sub>2</sub> O Monomer	3726.5	3725.7 <sup>S4</sup>
H <sub>2</sub> O Dimer	3715.5	3714.4 <sup>S4</sup>
H <sub>2</sub> O Dimer	3699.5	3697.7 <sup>S4</sup>
H <sub>2</sub> O Polymer	3688.9	3688 <sup>S4</sup>
H <sub>2</sub> O Monomer	3633.9	3632.5 <sup>S4</sup>
H <sub>2</sub> O Dimer	3546.6	3547.5 <sup>S4</sup>
H <sub>2</sub> O Polymer	3511.2	3510 <sup>S4</sup>
v <sub>3</sub> (CO <sub>2</sub> ) <sub>2</sub>	2350.9	
$v_3 CO_2$	2348.7	2348.6 <sup>S2</sup>
v <sub>3</sub> <sup>13</sup> CO <sub>2</sub>	2283.2	2282.8 <sup>S2</sup>
$v_3 NO_2$	2235.5	2235.55 <sup>S5</sup>
NO	1874.5	1874.3 <sup>S5</sup>
H <sub>2</sub> O Monomer	1598.5	1596.9 <sup>S4</sup>
v <sub>2</sub> (CO <sub>2</sub> ) <sub>2</sub>	663.7	
$v_2 CO_2$	662.3	662.3 <sup>S2</sup>

**Table S3:** Mid-infrared bands of atmospheric trace gases trapped in solid air at 15 K (from the experiment shown in Figure S8). Reference values pertain to the nitrogen matrix.

#### Results of MI-IR spectroscopy of isolated air (carbon dioxide in nitrogen-oxygen-argon)

#### Assignment of all observed species in the spectra of isolated air

In the matrix isolation experiment of Innsbruck air at 15 K, we observed several bands (cf. Figure S8) that can be assigned easily based on literature matrix isolation experiments. Specifically, we identified multiple complexes of carbon dioxide, nitrogen, and water. Tursi et al. <sup>S4</sup> already assigned most of the water signals in a nitrogen matrix. In accordance with their work, we were able to assign the peaks that we measured to the respective water mono-, di- and polymers. Besides the bands for H<sub>2</sub>O and the CO<sub>2</sub> bands described extensively in the manuscript, we also observed NO and NO<sub>2</sub> (cf. Table S3). The nitrogen oxides that we measured originated most likely from traffic pollution, which was always present due to the proximity of a much-frequented road (Innrain 52, Innsbruck, Austria on November 15, 2020). With the help of the work from Bahou et al. <sup>S5</sup>, we are able to assign these species to the signals at 2235.5 (v<sub>3</sub> NO<sub>2</sub>) cm<sup>-1</sup> and 1874.5 cm<sup>-1</sup> (NO<sup>-</sup>).

#### Dimer contribution to the absorption cross-sections in the air experiments

The bands in the isolated air spectrum are much broader than their counterparts in the Ne spectrum, but still are narrow enough to originate from single molecules. The broadness is owing to the more complex cages and the stronger interaction of the trapped species with  $N_2/O_2/Ar$  than with Ne. This made it more difficult to identify dimer and monomer bands. Yet, this was possible based on the calculations and the observations in Ne matrix. To disentangle monomer and dimer contributions to each band we used a Gaussian decomposition procedure. This procedure then also allowed us to retrieve band areas, just like in the Ne experiment. Again, by comparing the area of the decomposed peaks, we could estimate the fraction of  $(CO_2)_2$  that is present in matrix-isolated Innsbruck air. The information is summarized in Figure S9). Similar to the conclusions from the Ne experiment we also found dimer band areas amounting to 15%.

This conclusion rests on a three-peak decomposition in the stretching region (see Figure S9), where the Gaussian centered at 2350.9 cm<sup>-1</sup> pertains to the  $(CO_2)_2$  dimer and the Gaussian at 2348.8 cm<sup>-1</sup> and 2347.5 cm<sup>-1</sup> to the v<sub>3</sub> mode of CO<sub>2</sub> monomers trapped in two different cage geometries. In the bending region, we were also able to identify three different Gaussians. Similar to the stretching region, it was not possible to decompose the peak into only two different peaks. The Gaussians at 663.5 cm<sup>-1</sup> and 663.1 cm<sup>-1</sup> originate from the  $(CO_2)_2$  dimer and the one at 662.3 cm<sup>-1</sup> from the v<sub>2</sub> CO<sub>2</sub> monomer signal. Those peaks have already been described by <sup>S2</sup> for pure nitrogen matrices, except for the one at 663.1 cm<sup>-1</sup>. Noticing the proximity to the known dimer band and the same intensity of the Gaussians at 663.5 cm<sup>-1</sup> and 663.1 cm<sup>-1</sup> hints to an assignment as dimer band, where the small shift of 0.4 cm<sup>-1</sup> is again most likely caused by differing cage geometries.



**Figure S9.** Gaussian decomposition of the  $v_2$  and  $v_3$  peak of carbon dioxide in isolated air. The assignment corresponds to what is observed in pure nitrogen [a] in ref. <sup>S2</sup> and [b] in ref. <sup>S3</sup>.

# **Supplementary References**

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