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M Klarenaar, R Engeln, M van den Bekerom, M. C. M. van de Sanden, A Morillo-Candas, et al.. Time evolution of vibrational temperatures in a CO<sub>2</sub> glow discharge measured with infrared absorption spectroscopy. *Plasma Sources Science and Technology*, 2017, 26 (11), 10.1088/1361-6595/aa902e . hal-01898526

**HAL Id: hal-01898526**

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Submitted on 1 Mar 2024

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**Citation for published version (APA):**

Klarenaar, B. L. M., Engeln, R., van den Bekerom, D. C. M., Van De Sanden, M. C. M., Morillo-Candas, A. S., & Guaitella, O. (2017). Time evolution of vibrational temperatures in a CO<sub>2</sub> glow discharge measured with infrared absorption spectroscopy. *Plasma Sources Science and Technology*, 26(11), Article 115008.  
<https://doi.org/10.1088/1361-6595/aa902e>

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**DOI:**  
[10.1088/1361-6595/aa902e](https://doi.org/10.1088/1361-6595/aa902e)

**Document status and date:**  
Published: 01/11/2017

**Document Version:**  
Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

**Please check the document version of this publication:**

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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# Time evolution of vibrational temperatures in a CO<sub>2</sub> glow discharge measured with infrared absorption spectroscopy

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Received 7 July 2017, revised 26 September 2017

Accepted for publication 2 October 2017

Published 26 October 2017



CrossMark

## Abstract

Vibrational temperatures of CO<sub>2</sub> are studied in a pulsed glow discharge by means of time-resolved *in situ* Fourier transform infrared spectroscopy, with a 10 μs temporal resolution. A method to analyze the infrared transmittance through vibrationally excited CO<sub>2</sub> is presented and validated on a previously published CO<sub>2</sub> spectrum, showing good agreement between fit and data. The discharge under study is pulsed with a typical duty cycle of 5–10 ms on–off, at 50 mA and 6.7 mbar. A rapid increase of the temperature of the asymmetric stretch vibration ( $T_3$ ) is observed at the start of the pulse, reaching 1050 K, which is an elevation of 550 K above the rotational temperature ( $T_{\text{rot}}$ ) of 500 K. After the plasma pulse, the characteristic relaxation time of  $T_3$  to  $T_{\text{rot}}$  strongly depends on the rotational temperature. By adjusting the duty cycle, the rotational temperature directly after the discharge is varied from 530 to 860 K, resulting in relaxation times between 0.4 and 0.1 ms. Equivalently, as the gas heats up during the plasma pulse, the elevation of  $T_3$  above  $T_{\text{rot}}$  decreases strongly.

Keywords: carbon dioxide plasma, glow discharge, vibrational temperature, Fourier transform infrared spectroscopy

## 1. Introduction

Efficient reduction of CO<sub>2</sub> to CO is a key step in the process of storing renewable energy in the form of hydrocarbon fuels [1–4]. A promising route for this dissociation process is through selective excitation of the asymmetric stretch vibration of CO<sub>2</sub> in a non-equilibrium plasma [5–7]. Studies on vibrational excitation of CO<sub>2</sub> are often done in the field of CO<sub>2</sub> lasers, reporting vibrational temperatures which are elevated with

respect to the translational temperature [8–11]. These measurements are performed in continuous glow discharges, determining vibrational excitations depending on e.g. gas composition, pressure, plasma current, and reduced electric field. Time-resolved measurements on pulsed CO<sub>2</sub> discharges are only rarely performed [12]. However, such measurements could give detailed insight into the time evolution of vibrational state densities, including excitation and relaxation times, and can be used for comparison and validation of (rate constants used in) kinetic models of CO<sub>2</sub> discharges.

When studying the vibrational excitation of CO<sub>2</sub>, all vibrational modes should be taken into account. Quantum numbers  $\nu_1$ ,  $\nu_2$ , and  $\nu_3$  are used to represent the symmetric stretch, doubly degenerate bending, and asymmetric stretch mode, respectively. Additionally, the contribution of  $\nu_2$  to the angular momentum is described using number  $l_2$ . Since the

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energy of one  $\nu_1$  quantum and two  $\nu_2$  quanta is almost equal, and their symmetry is the same if  $\nu_2$  does not contribute to the angular momentum, there is a strong Fermi resonance between states of the form  $(\nu_1, \nu_2^2, \nu_3)$  and  $((\nu_1 - 1), (\nu_2 + 2)^2, \nu_3)$  [13–15].

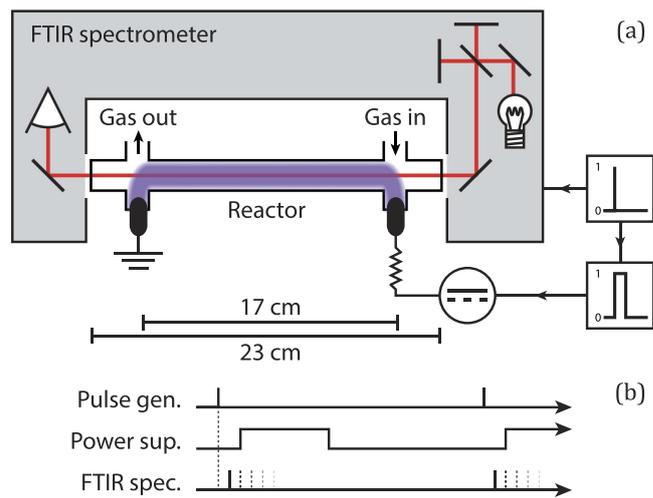
Possible methods for detecting vibrational state densities include spontaneous Raman scattering [16, 17] and coherent anti-Stokes Raman scattering [18, 19]. These spatially and time-resolved techniques are well suited to determine Raman active vibrations, like those of CO, O<sub>2</sub>, and N<sub>2</sub>. For CO<sub>2</sub>, however, only the symmetric stretch mode is Raman active [20], hence the densities of the asymmetric stretch mode (and bending mode) cannot be determined. On the other hand, these modes are strongly IR active [20] and therefore it is possible to determine the vibrational state densities using IR emission spectroscopy [16, 21, 22]. However, reabsorption of emitted IR radiation by the optically thick CO<sub>2</sub> makes it particularly difficult to determine densities deeper inside the discharge.

Using IR absorption spectroscopy, one is able to accurately determine vibrational state densities inside the plasma over several orders of magnitude. To this purpose, tunable diode lasers (TDL) are used as an IR source to determine densities in CO<sub>2</sub> lasers [9, 11]. Although TDLs can scan mode hop free only very narrow frequency ranges (in the order of single wavenumbers), a well selected range can contain absorption lines of multiple vibrational levels. Unfortunately, the nature of operation prohibits easy implementation of time-resolved measurements. The quickly pulsed and chirped (several wavenumbers) quantum cascade laser is a good alternative, but has its own challenge in the form of the peak-distorting rapid passage effect [23].

To combine the ability of doing time-resolved measurements with measuring IR absorption over a wider wavenumber range, we use *in situ* Fourier transform infrared (FTIR) spectroscopy. Rivallan *et al* [12] already showed its suitability to detect time-resolved absorption lines in a glow discharge using an air/CO<sub>2</sub> mixture. We exploit the homogeneity of the positive column of the glow discharge [24] to study the time evolution of the vibrational temperatures of CO<sub>2</sub> and CO (formed in the discharge), during plasma ignition, development to steady state, and during relaxation directly after the plasma pulse.

## 2. Experimental methods

The experimental setup is schematically shown in figure 1(a). The plasma reactor is made of Pyrex and is cylindrically shaped with an inner diameter of 2 cm and a length of 23 cm, with BaF<sub>2</sub> windows at the sides. The electrodes and gas in- and outlet are both 17 cm apart. A 50 mA DC current is achieved by connecting a 50 k $\Omega$  resistor in series and applying 4.0 kV (2.5 kV over the resistor and 1.5 kV over the reactor). A high-voltage probe (LeCroy, PPE 20kV) and an oscilloscope (LeCroy, LT584M) are used to monitor the voltage. The power supply is triggered using a pulse generator (TTi, TGP110), resulting in



**Figure 1.** (a) The FTIR spectrometer, including the plasma reactor, positioned in the sample compartment. A pulse generator is used to simultaneously trigger the step-scan mode of the spectrometer and the square DC pulse for the plasma. The trigger scheme is shown in (b).

square pulses with rise and fall times in the order of a couple  $\mu$ s. The plasma is pulsed with a typical time of 5–10 ms on–off. A basic trigger scheme is shown in figure 1(b).

The incoming gas consists of pure CO<sub>2</sub> (Air Liquide, *Alphagaz 1*) and the gas flow is controlled at 7.4 sccm using a mass flow controller (Bronkhorst, F-201CV). Pressure is maintained at 6.7 mbar with a scroll pump (Edwards, XDS5) and a manual valve, while the pressure is measured using a pressure gauge (Pfeiffer, CMR 263). With the reactor dimensions as mentioned earlier, the gas residence time is in the order of seconds.

The reduced electric field under these conditions is estimated by using a similar reactor, equipped with two metal rods radially pointing inside the positive column of the reactor. Measuring the potential difference over the rods while maintaining a continuous discharge of 50 mA at 6.7 mbar gives a reduced field of 60 Td. The electron number density is then calculated, using table 1 in [25] for the electron drift velocity, to be  $10^{10}$  cm<sup>-3</sup>.

The reactor is positioned in the sample compartment of an FTIR spectrometer (Bruker, *Vertex 70*), shown in figure 1(a). Time resolved measurements are performed by operating the spectrometer in the step-scan mode. In this mode, the interferometer assumes a position, relaxes for 60 ms, and awaits a trigger signal, e.g. from a pulse generator. After receiving a trigger, the DC signal of the IR detector (MCT) is repetitively read out with a period of 10  $\mu$ s, hence, 1100 repetitions result in a measured time period of 11 ms. Four trigger series are averaged per interferometer position (53, 323 in total), whereafter the interferometer moves to the next position and the procedure is repeated, building a 2D interferogram. Fourier transforming the interferogram gives a time-resolved intensity spectrum with a 10  $\mu$ s resolution and a spectral resolution of 0.2 cm<sup>-1</sup>. A trigger scheme including the pulse generator, the gating of the power supply of the reactor, and the read-out by the IR detector is shown in figure 1(b).

The infrared light that reaches the detector is a combination of three contributions:

- Light emitted by the IR source of the spectrometer, going through the interferometer, then through the reactor towards the detector.
- Spontaneous emission from the plasma that is directly emitted towards the detector.
- Spontaneous emission from the plasma that first enters the interferometer and is reflected back through the reactor towards the detector.

To be able to study the light absorption from the IR source through the reactor, the intensity spectrum should be corrected for other spectrally resolved contributions. Light that is emitted from the plasma directly towards the detector only induces an interferogram offset, which is not apparent after Fourier transformation. On the other hand, plasma emission that is reflected by the interferometer is spectrally resolved: it depends on the mirror position of the interferometer which frequencies are reflected. The intensity spectrum should be corrected for this and accordingly a time-resolved measurement is performed while blocking all light from the IR source, revealing only the plasma emission.

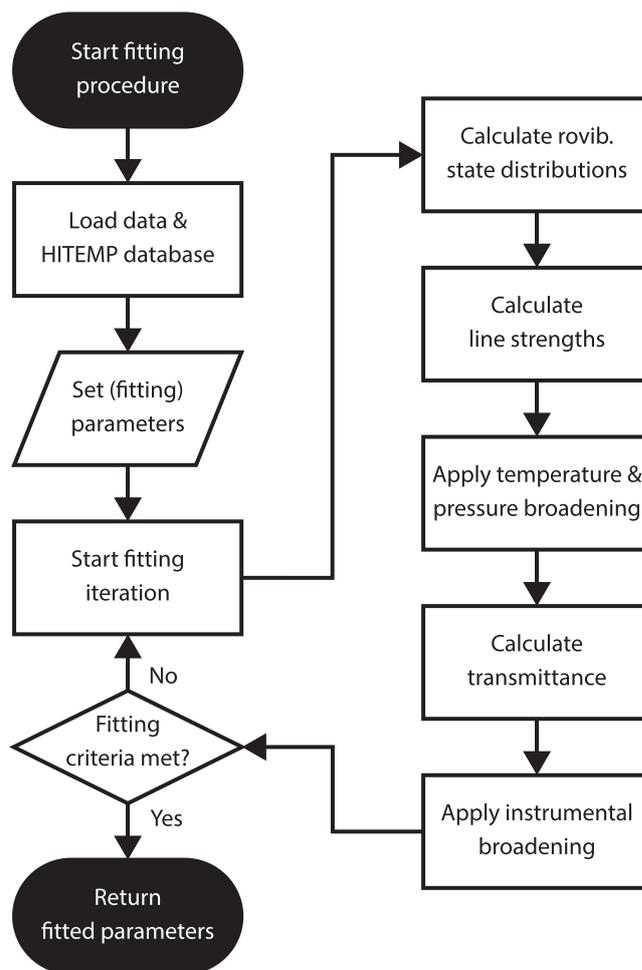
After subtracting the emission from the intensity spectrum, the time-resolved transmittance is calculated by dividing the remainder by the spectral profile of the IR source. This common background is taken after purging the reactor with nitrogen and operating the FTIR spectrometer in its conventional mode. The spectral region between 1975 and 2400  $\text{cm}^{-1}$  contains lines of both CO and asymmetric-stretch transitions of CO<sub>2</sub> and is analyzed using the fitting algorithm, discussed in the next section.

### 3. Computational algorithm

#### 3.1. Database and fitting parameters

The measured FTIR spectra result from infrared absorption by a molecular population which is not in thermal equilibrium. To be able to accurately analyze these spectra, an algorithm has been developed to calculate and fit these non-equilibrium infrared transmittance spectra. The basic flowchart for the algorithm can be seen in figure 2.

The algorithm makes use of the HITEMP-2010 database [26], which contains transition energies, Einstein A coefficients, broadening constants, etc, of a wide variety of molecules. Transition data for CO<sub>2</sub> is available up to  $\nu_3 = 6 \rightarrow 7$ , while vibrational transitions of CO are documented as far as  $\nu_{\text{CO}} = 14 \rightarrow 15$ . Transitions of both these vibrational quanta (i.e.  $(\nu_1, \nu_2^1, \nu_3) \rightarrow (\nu_1, \nu_2^1, \nu_3 + 1)$  and  $(\nu_{\text{CO}}) \rightarrow (\nu_{\text{CO}} + 1)$ ) are present in the region of interest of 1975–2400  $\text{cm}^{-1}$ . The rotationless transition energies of the ground state to the first level are centered around 2349  $\text{cm}^{-1}$  and 2143  $\text{cm}^{-1}$ , for CO<sub>2</sub> and CO, respectively [13, 27]. Depending on the measurement conditions, the CO and CO<sub>2</sub> lines will partially overlap. Hence, in an accurate analysis CO should be included.



**Figure 2.** A calculation diagram of the developed algorithm to compute and fit non-equilibrium infrared transmittance spectra. The left hand column represents the preparation of the calculation, including the users choice (parallelogram) of to be fitted parameters. The fitting iteration process that involves the calculation of the spectra, is elaborated in the right hand column. The fit is completed when one of the function, step, or optimality tolerances is satisfied, all with a relative value of  $10^{-6}$ .

**Table 1.** List of fitting parameters, including symbol, description, and guess value for the fit.

Symbol	Description	Guess
$T_{\text{rot}}$	Rotational temperature	600 K
$T_{1,2}$	$\nu_{1,2}$ temperature of CO <sub>2</sub>	600 K
$T_3$	$\nu_3$ temperature of CO <sub>2</sub>	600 K
$T_{\text{CO}}$	Vib. temperature of CO	600 K
$c_{T_{\text{th}}}$	Thermal variable	0.1
$\alpha$	CO <sub>2</sub> conversion factor	0.3
$p$	Pressure	Var.

Before continuing to calculate a spectrum, several parameters have to be set. Table 1 shows the parameters that are included in the fit. The rotational temperature  $T_{\text{rot}}$  is assumed to be the same for molecules of CO<sub>2</sub> and CO, and equal to the translational temperature [9]. The vibrational temperature, however, is split into different parameters. Since modes  $\nu_1$

and  $\nu_2$  of CO<sub>2</sub> are Fermi coupled, they are described with one temperature,  $T_{1,2}$  [13]. For the asymmetric stretch mode  $T_3$  is used, and  $T_{CO}$  is used for the vibrational temperature of CO.

Absorption spectroscopy is a line-of-sight technique, i.e. under the present experimental conditions measured spectra result from absorption over the full length of the reactor. As figure 1 shows, this length is not completely filled by the discharge, resulting in two greatly different temperature regions: thermal gas and non-thermal plasma. Therefore,  $f_{th}$ , the volume fraction of thermal gas is introduced. For the analysis in this study, this fraction is fixed at  $(23-17 \text{ cm})/23 \text{ cm} \approx 0.26$ , based on the length of the reactor and the positioning of the electrodes.  $T_{th}$  describes the translational energy and rovibrational densities in this volume, having a lower and upper limit of 273 K and  $T_{rot}$ , respectively, and is fitted using thermal variable  $c_{T_{th}}$  ( $0 \leq c_{T_{th}} \leq 1$ ):

$$T_{th} = c_{T_{th}} \cdot (T_{rot} - 273) + 273. \quad (1)$$

To calculate the number densities of molecules in the thermal and non-thermal region,  $n_{th}$  and  $n_{nth}$ , respectively, it is assumed that the pressure in both parts is equal,  $p$ . Additionally, in the non-thermal part the translational temperature is assumed to be equal to the rotational temperature. Using the ideal gas law results in equations (2) and (3):

$$n_{th,eff} = f_{th} n_{th} = f_{th} \frac{p}{k_B T_{th}}, \quad (2)$$

$$n_{nth,eff} = (1 - f_{th}) n_{nth} = (1 - f_{th}) \frac{p}{k_B T_{rot}}, \quad (3)$$

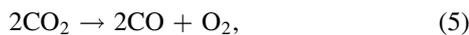
where  $k_B$  is the Boltzmann constant.  $n_{th,eff}$  and  $n_{nth,eff}$  are, respectively, the effective thermal and non-thermal number densities, i.e. the apparent number densities over the full line-of-sight of the absorption measurement.

The molecular fractions of CO<sub>2</sub> and CO are calculated using conversion factor  $\alpha$ , defined as

$$\alpha = \frac{[CO]}{[CO] + [CO_2]}, \quad (4)$$

where  $[CO_2]$  and  $[CO]$  are the molecular concentrations of CO<sub>2</sub> and CO, respectively. It is expected that towards the exhaust of the reactor the concentration of CO increases. However, the spatial profile is unclear and will be studied in future work. In the fitting model, the molecular fractions of CO<sub>2</sub> and CO are therefore treated as invariant over the length of the reactor and equal in both the thermal and non-thermal part. Fitted values of  $\alpha$  should be regarded as spatially averaged.

Other than CO<sub>2</sub> and CO, IR transmittance spectra reveal only insignificant amounts of O<sub>3</sub> (O<sub>2</sub> is not IR active). Therefore, following the dissociation reaction



it is assumed that for every two CO molecules, one O<sub>2</sub> molecule is present in the reactor. This results in equations (6) and (7) for the molecular fractions of CO<sub>2</sub> and CO, accordingly:

$$f_{CO_2} = \frac{1 - \alpha}{1 + \alpha/2}, \quad (6)$$

**Table 2.** List of values for  $B$  (cm<sup>-1</sup>),  $D$  (10<sup>-6</sup> cm<sup>-1</sup>), and  $H$  (10<sup>-12</sup> cm<sup>-1</sup>) for CO<sub>2</sub> and CO, calculated from [14, 33, 34].

Isotopologue	$B$	$D$	$H$
<sup>12</sup> C <sup>16</sup> O <sub>2</sub> [14]	0.39022	0.1333	0.0090
<sup>13</sup> C <sup>16</sup> O <sub>2</sub> [14]	0.39024	0.1332	0.0090
<sup>16</sup> O <sup>12</sup> C <sup>18</sup> O [14]	0.36819	0.1187	0.0075
<sup>16</sup> O <sup>12</sup> C <sup>17</sup> O [14]	0.37862	0.1255	0.0082
<sup>12</sup> C <sup>16</sup> O [33]	1.9225	6.121	5.7
<sup>13</sup> C <sup>16</sup> O [34]	1.8380	5.593	5.5
<sup>12</sup> C <sup>18</sup> O [34]	1.8310	5.550	4.9

$$f_{CO} = \frac{\alpha}{1 + \alpha/2}. \quad (7)$$

To calculate the molecular number densities of thermal and non-thermal CO<sub>2</sub> and CO, these fractions should be multiplied by equations (2) and (3).

### 3.2. Calculating the spectrum

**3.2.1. Calculate rovibrational state distributions.** After defining the fitting parameters the fitting process is started. The first step in constructing a transmittance spectrum is calculating the thermal and non-thermal rovibrational state distributions. For this, it is assumed that energies of rotational levels and energies of different vibrational modes are independent. In literature, this is a widely used approximation, though it should be noted that it becomes less accurate for higher vibrational states [9, 28–30].

The population  $N_s$  of state  $s$ , having rotational state  $J$  and vibrational state(s)  $\nu_i$ , can then be calculated, using:

$$N_s = N \phi_{rot,J} \prod_i \phi_{vib,\nu_i}. \quad (8)$$

Here,  $N$  is the total number of molecules per unit volume and  $i$  is an index for vibrational modes (i.e. 1, 2, and 3 for CO<sub>2</sub>, while CO only has one vibrational mode).  $\phi_{rot,J}$  and  $\phi_{vib,\nu_i}$  are the fraction of molecules in the rotational state and vibrational state(s) of  $s$ , respectively.

$\phi_{rot,J}$  is calculated assuming a Boltzmann distribution:

$$\phi_{rot,J} = \frac{g_{rot,J}}{Q_{rot}} \exp\left(-\frac{hcE_{rot,J}}{k_B T_{rot}}\right), \quad (9)$$

where  $h$ ,  $c$ , and  $k_B$  are the Planck constant, the speed of light, and the Boltzmann constant, respectively. The energy  $E_{rot,J}$  of rotational state  $J$  is calculated using the rotational constant  $B$ , centrifugal distortion constant  $D$ , and third order correction factor  $H$  as listed for all isotopologues of CO<sub>2</sub> and CO that are included in the algorithm, in table 2. The rotational degeneracy  $g_{rot,J}$  is a product of the factor  $(2J + 1)$  and a rotational-state-dependent and -independent weight, which can be found for different isotopologues in [31]. The rotational partition sum  $Q_{rot}$  is calculated such that  $\phi_{rot,J}$  is normalized and its sum over all  $J$  is equal to one, as done in McDowell *et al* [32].

Going back to equation (8), in the plasma a Treanor distribution is assumed for vibrational states, which Dang

**Table 3.** List of values for  $G_1$  and  $\omega_e x_e$  (both in  $\text{cm}^{-1}$ ) for  $\text{CO}_2$  (see footnote 5) and CO, calculated from [14, 33, 34].

Isotopologue	Mode	$G_1$	$\omega_e x_e$
$^{12}\text{C}^{16}\text{O}_2$ [14]	$\nu_1$	1333.93	2.93
	$\nu_2$	667.47	-0.38
	$\nu_3$	2349.16	12.47
$^{13}\text{C}^{16}\text{O}_2$ [14]	$\nu_1$	1334.32	2.93
	$\nu_2$	648.63	-0.37
	$\nu_3$	2283.49	11.71
$^{16}\text{O}^{12}\text{C}^{18}\text{O}$ [14]	$\nu_1$	1295.72	2.76
	$\nu_2$	662.47	-0.39
	$\nu_3$	2332.15	12.34
$^{16}\text{O}^{12}\text{C}^{17}\text{O}$ [14]	$\nu_1$	1296.04	2.76
	$\nu_2$	643.44	-0.36
	$\nu_3$	2265.98	11.59
$^{12}\text{C}^{16}\text{O}$ [33]	$\nu_{\text{CO}}$	2143.24	13.29
$^{13}\text{C}^{16}\text{O}$ [34]	$\nu_{\text{CO}}$	2096.03	12.70
$^{12}\text{C}^{18}\text{O}$ [34]	$\nu_{\text{CO}}$	2092.09	12.65

*et al* [9] experimentally confirmed to be accurate up to  $\nu_3 = 9$  in very similar glow discharges [35]. It should be noted that the Treanor distribution overestimates the population of higher energy levels, close to the dissociation energy [35, 36]. However, in the conditions under study, only states up to  $\nu_3 = 4$  show a contribution to the transmittance above noise level, well below the dissociation limit.  $\phi_{\text{vib},\nu_i}$  then becomes:

$$\phi_{\text{vib},\nu_i} = \frac{g_{\text{vib},\nu_i}}{Q_{\text{vib},i}} \exp\left(-\frac{hc}{k_B} \left( \nu_i \frac{G_{1,i}}{T_i} - \nu_i(\nu_i - 1) \frac{\omega_e x_{e,i}}{T_{\text{rot}}} \right)\right). \quad (10)$$

Here,  $g_{\text{vib},\nu_i}$  is the degeneracy of vibrational mode  $\nu_i$  (for  $\text{CO}_2$   $g_{\text{vib},\nu_1} = g_{\text{vib},\nu_3} = 1$ ,  $g_{\text{vib},\nu_2} = \nu_2 + 1$  and for CO  $g_{\text{vib},\nu_{\text{CO}}} = 1$ ).  $G_{1,i}$  is the energy spacing between the ground and first vibrational level, and  $\omega_e x_{e,i}$  is the anharmonicity, listed in table 3 for the isotopologues of  $\text{CO}_2$  and<sup>5</sup> CO that are included in the algorithm. Cross terms are not taken into account, since the vibrational modes are treated as independent. It is inherent to the Treanor distribution that the harmonic part is scaled with vibrational temperature  $T_i$  ( $= [T_{1,2}, T_{1,2}, T_3, T_{\text{CO}}]$  for  $i = [1, 2, 3, \text{CO}]$ ), while the anharmonic part is scaled with the translational temperature. In equation (10) the translational temperature is substituted by  $T_{\text{rot}}$ , under the previously made assumption that these temperatures are equal. When for thermal gas  $T_i = T_{\text{rot}} = T_{\text{th}}$ , equation (10) reduces back to a Boltzmann distribution.

Similar to the rotational partition sum, the partition sum of vibrational modes  $Q_{\text{vib},i}$  is determined such that the

<sup>5</sup> For values of  $\nu_2$  a full contribution of angular momentum is included (i.e.  $l_2 = \nu_2$ ). Furthermore, Fermi resonance between  $(\nu_1, \nu_2^2, \nu_3)$  and  $((\nu_1 - 1), (\nu_2 + 2)^2, \nu_3)$  induces a Fermi-level dependent energy shift which is not included in the listed values for  $\nu_1$ . In the fitting algorithm, these shifts are calculated as described in [14, 15].

fractions  $\phi_{\text{vib},\nu_i}$  are normalized:

$$\sum_{\nu_i=0}^{\nu_{i,\text{max}}} \phi_{\text{vib},\nu_i} = 1. \quad (11)$$

Here,  $\nu_{i,\text{max}}$  is the maximum vibrational state taken into account ( $\nu_{i,\text{max}} = [40, 70, 30, 35]$  for  $i = [1, 2, 3, \text{CO}]$ ), chosen such that all levels up to at least 6 eV are included in the calculation. It prevents the normalization being significantly influenced by the previously mentioned overpopulation of higher vibrational states resulting from the Treanor distribution.

**3.2.2. Calculate line strengths.** The next step is the calculation of the line strength, starting from the Einstein A coefficient  $A_{ul}$  for spontaneous emission from upper state u to lower state l. This coefficient is listed in the HITEMP database. The line strength  $S_j$  of transition  $j$  can be calculated as follows [31]:

$$S_j = \frac{I_a g_{\text{rot},u} A_{ul}}{8\pi c \tilde{\nu}_j^2} \left( \frac{N_l}{g_l N} - \frac{N_u}{g_u N} \right), \quad (12)$$

where  $I_a$  is the fractional abundance of the isotopologue as listed in [31],  $\tilde{\nu}_j$  is the transition energy as listed in the HITEMP database, and  $g_l$  and  $g_u$  are the total rovibrational degeneracy of the lower and upper state, respectively<sup>6</sup>. Equation (8) is now used to compute the lower and upper state densities,  $N_l$  and  $N_u$ , respectively.

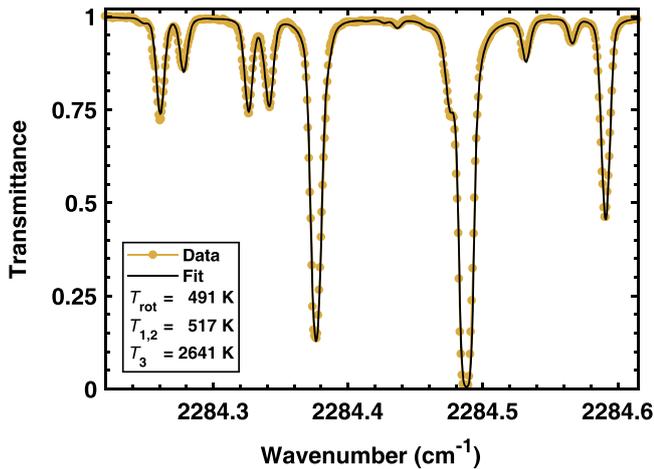
Although equation (12) is derived using the relations between spontaneous emission and stimulated emission and absorption coefficients under the assumption of thermal-equilibrium black-body radiation, it is also valid in situations where there is no thermal equilibrium [37].

**3.2.3. Apply temperature and pressure broadening.** The HITEMP database lists for each line a self- and air-broadened half-width, as well as a  $\text{CO}_2$ -broadened half-width for CO. Broadening due to pressure from other molecular species is approximated as if it were from air. The Lorentzian pressure broadening profile is convolved with the Gaussian shaped Doppler broadening and multiplied by the line strength  $S_j$ . This results in a Voigt-shaped cross section  $\sigma_j(\tilde{\nu})$ , unique for every line  $j$  [38, 39]. The Voigt shape is applied using the empirical expression by Whiting [39, 40].

**3.2.4. Calculate transmittance.** The transmittance  $T_{\tilde{\nu}}$  is calculated using the Beer–Lambert law [29]:

$$T_{\tilde{\nu}} = \prod_{n=n_{\text{th,eff}}}^{n_{\text{th,eff}}} \prod_{f=f_{\text{CO}}}^{f_{\text{CO}_2}} \exp\left(-L n f \sum_{j=1}^{j_{\text{max}}} \sigma_j(\tilde{\nu})\right), \quad (13)$$

<sup>6</sup> It would be physically accurate to replace the rotational degeneracy  $g_{\text{rot},u}$  in equation (12) by the total degeneracy  $g_u$ . However,  $g_{\text{rot},u}$  is used because of how  $A_{ul}$  is determined in the HITEMP database [31].



**Figure 3.** A fit, using the algorithm, on CO<sub>2</sub> data from Dang *et al* [9]. Transmission data is digitally extracted from the article and divided by an artificial background.

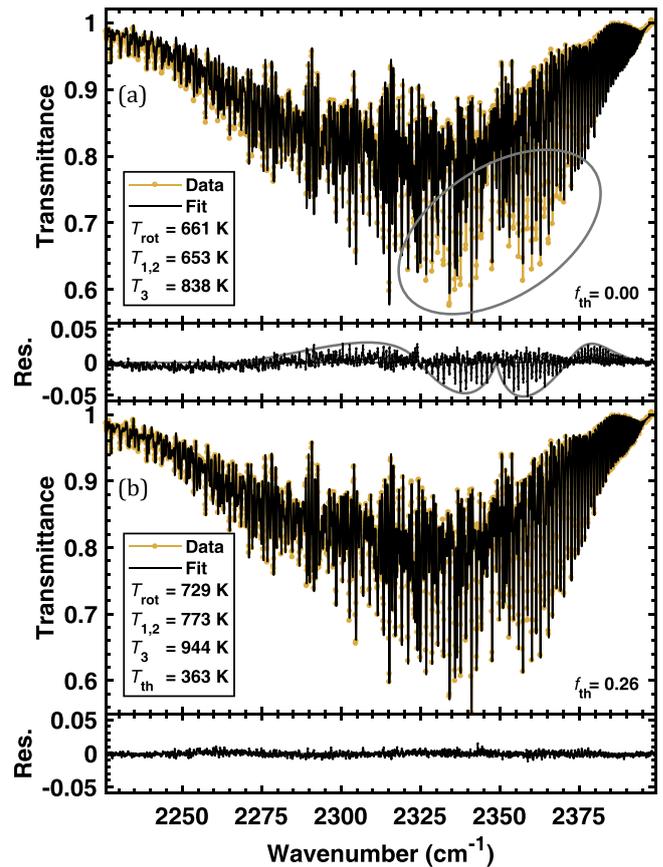
where  $L$  is the length of the reactor. The transmittance is constructed from a product of four exponents, i.e. the contributions of thermal and non-thermal CO<sub>2</sub> and CO.

**3.2.5. Apply instrumental broadening.** In the last step, the broadening of the instrument is applied. The final transmittance is obtained by convolving  $T_p$  with the instrumental line shape of the FTIR. A three-term Blackman–Harris is used as the apodization function for the Fourier transform, resulting in a spectral line shape which can be very well approximated by a Gaussian [41]. For the spectrometer settings used in this study, the full-width at half-maximum of this Gaussian is determined to be  $0.27 \text{ cm}^{-1}$ .

### 3.3. Validation of the algorithm

The computational algorithm is tested on non-thermal data, obtained from literature. Dang *et al* [9] performed IR absorption measurements on a glow discharge in a gas mixture of 10% CO<sub>2</sub>, 38% N<sub>2</sub>, and 52% He at a pressure of 20 mbar and a plasma current of 10 mA. They used a diode as an infrared source, resulting in a very narrow scanning range from 2284.2 to 2284.6  $\text{cm}^{-1}$ . The transmission graph they provided in [9] has been digitally extracted and divided by an artificial background, resulting in the transmittance in figure 3. All features in the spectrum originate from transitions in CO<sub>2</sub>, since N<sub>2</sub> and He are not IR active, while CO, which is formed in the plasma, is not active in this wavenumber region.

The spectrum is fitted using the algorithm, not including any thermal gas, nor instrumental broadening, since this broadening is not significant in regard to temperature and pressure broadening when using a diode as an IR source. The best fit, which is shown in figure 3, is obtained with  $T_{\text{rot}} = 491 \text{ K}$ ,  $T_{1,2} = 517 \text{ K}$ , and  $T_3 = 2641 \text{ K}$ . Although Dang *et al* do not provide temperatures for this measurement, a  $T_3$  elevation with respect to  $T_{\text{rot}}$  of 2150 K is comparable to those under similar conditions listed in [9], i.e. between 1500 and 2500 K.



**Figure 4.** Two fits on the same CO<sub>2</sub> and CO data at 2 ms in the discharge with a 5–10 ms on–off duty cycle at 50 mA and 6.7 mbar. In panel (a)  $f_{\text{th}} = 0$ , assuming a non-thermal population over the whole reactor, while in (b)  $f_{\text{th}} = 0.26$ . The residual is shown on the same scale as the data.

## 4. Results

### 4.1. Adding thermal-volume fraction

Figure 4 shows a measurement taken at 2 ms in the discharge of a 5–10 ms on–off duty cycle of 50 mA at 6.7 mbar. The spectrum is fitted once with  $f_{\text{th}}$  set to 0 and once with the default value of 0.26, in order to illustrate the effect of adding a thermal-volume fraction to the calculation of the transmittance spectra. Both fits are respectively shown in panels (a) and (b), including residuals.

The effect of adding thermal gas is most visible around  $2349 \text{ cm}^{-1}$ , which is the central wavenumber of the line structure of the  $(0, 0^0, 0) \rightarrow (0, 0^0, 1)$  transition of <sup>12</sup>C<sup>16</sup>O<sub>2</sub>. In panel (a), symmetrically around this point an oval shape indicates a discrepancy between data and fit. This discrepancy is further exposed in the residual. The general shape of the residual is typical for a transmittance spectrum of CO<sub>2</sub> in the vibrational ground state, which is fitted with a too high rotational temperature.

In panel (b), this discrepancy has disappeared by adding to the fitting conditions that 26% of the gas in the reactor volume is thermal. The temperature of the thermal gas fraction is fitted at 363 K, while the rotational temperature of the non-thermal fraction increased from 661 K in (a) to 729 K in

(b). Also  $T_{1,2}$  and  $T_3$  from the fitted spectra significantly increase from (a) to (b). These temperatures largely represent the ratio of the ground state density over the density of vibrationally excited states. At temperatures below 400 K, thermally distributed  $\text{CO}_2$  and  $\text{CO}$  mainly populate the ground state (82% and 99.96%, respectively). Hence, if the thermal volume is not included in the fitting model, the ground-state density in the non-thermal part apparently increases, lowering the fitted vibrational temperatures.

#### 4.2. Fitting a time-resolved series

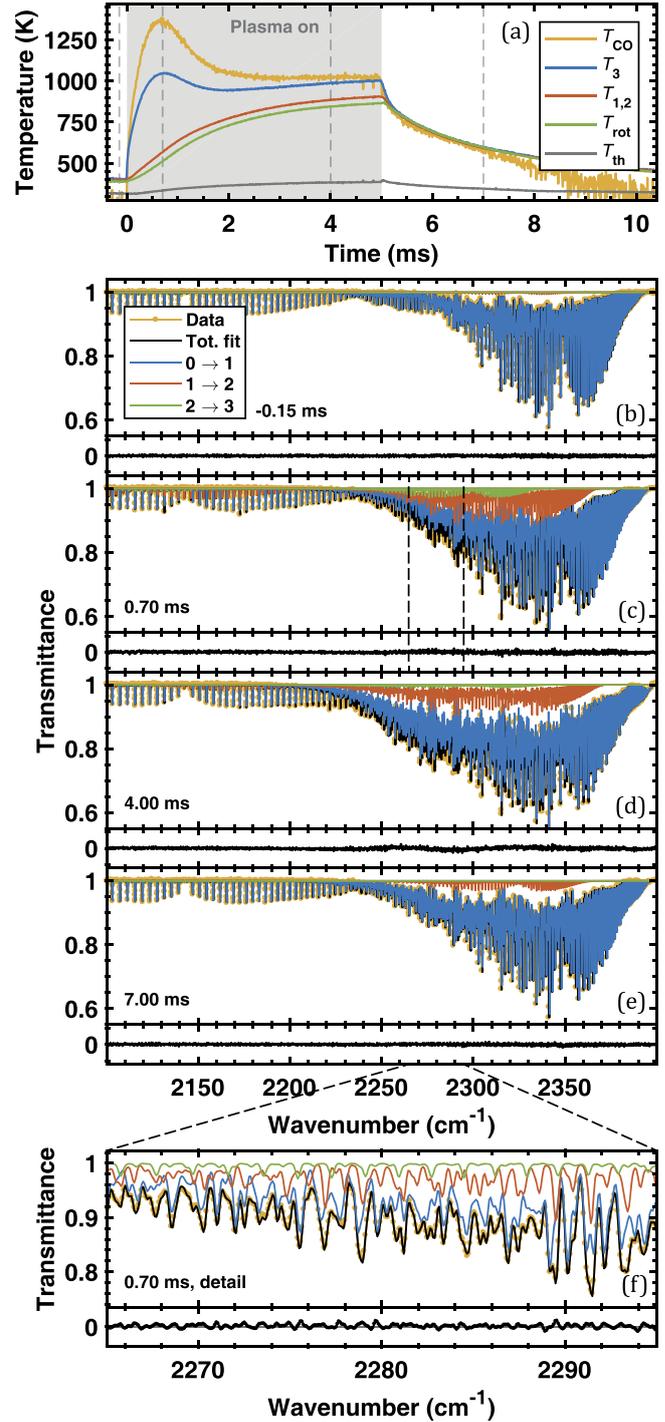
Figure 5 shows the time-resolved measurement series at 6.7 mbar, 50 mA, and a 5–10 ms on–off sequence. In panel (a), the fitted  $T_{\text{rot}}$ ,  $T_{1,2}$ ,  $T_3$ ,  $T_{\text{CO}}$ , and  $T_{\text{th}}$  are plotted versus time. The gray section marks the plasma-on phase. Panels (b)–(e) represent examples of the fitted spectra at the time points that are indicated by the dashed vertical lines in panel (a). The total fits are shown in black, while the colored spectra represent the individual contributions of transitions of the forms  $(\nu_1, \nu_2^j, \nu_3) \rightarrow (\nu_1, \nu_2^j, (\nu_3 + 1))$  and  $(\nu_{\text{CO}}) \rightarrow (\nu_{\text{CO}} + 1)$ . The residual of the total fit is included below each panel. Lines at energies larger than  $2235 \text{ cm}^{-1}$  mainly belong to  $\text{CO}_2$ , while lines of  $\text{CO}$  are mostly located below this energy. Panel (f) shows a detail of panel (c).

Panel (a) shows the temperature behavior as a function of time, and starts right before the plasma is switched on, with all temperatures of the non-thermal part in equilibrium at 400 K ( $T_{\text{CO}}$  is not sensitive around this temperature and is stuck at the lower fitting boundary of 273 K). At this temperature  $\nu_3$  state densities are very low, and accordingly, in panel (b) hardly any lines are visible for  $\nu_3 > 0$ . Hereafter,  $T_3$  and  $T_{\text{CO}}$  increase rapidly until a maximum is reached at 0.70 ms. In panel (c), this is seen as an increase of lines coming from  $\nu_3 = 1 \rightarrow 2$  and  $2 \rightarrow 3$ , and  $\nu_{\text{CO}} = 1 \rightarrow 2$ . Continuing in time,  $T_{\text{rot}}$  and  $T_{1,2}$  follow a similar growth and all temperatures of the non-thermal part develop towards a non-thermal equilibrium between 850 and 1050 K. In panel (d), at 4.00 ms, the  $\text{CO}_2$  and  $\text{CO}$  spectra become wider as a result from an increased density of higher rotational,  $\nu_1$ , and  $\nu_2$  states. At 5.00 ms the plasma turns off and the non-thermal-volume part equilibrates within tens of  $\mu\text{s}$ . In panel (e), a transmittance spectrum is shown at 7.00 ms, with all temperatures half-way relaxed towards the initial conditions in panel (b). The thermal temperature  $T_{\text{th}}$  only increases and decreases slightly during and after the pulse, staying between 300 and 400 K. During the full cycle, the fitted  $\text{CO}_2$  conversion factor  $\alpha$  stays practically constant around 0.18.

Before further discussion on the fitted temperatures, the fit of the calculated spectra to the data is studied in more detail. To this purpose, a parameter scan of several fitting parameters is performed while calculating the reduced chi-squared,  $\chi_{\text{red}}^2$  [42]:

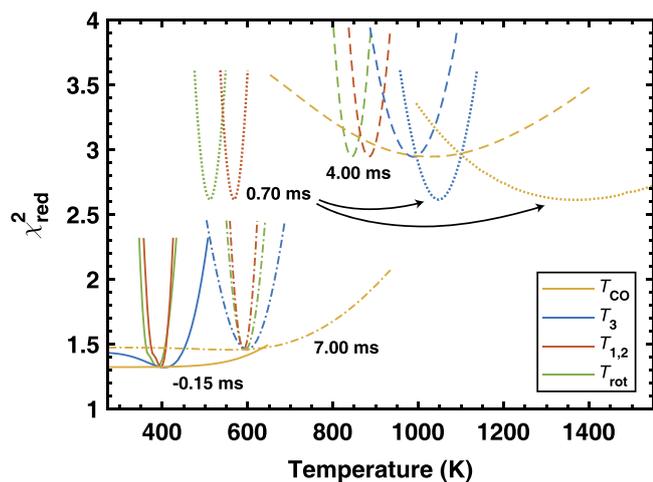
$$\chi_{\text{red}}^2 = \frac{1}{N - n} \sum_{i=1}^N \frac{(O_i - F_i)^2}{\sigma^2}. \quad (14)$$

Here,  $N$  is the number of wavenumber points,  $n$  is the number of fitting parameters, and  $O$  and  $F$  is the observed and fitted



**Figure 5.** A time-resolved measurement series at a pressure of 6.7 mbar, plasma current of 50 mA, and a 5–10 ms on–off sequence. Panel (a) shows the fitted temperatures versus time. The dashed lines indicate the time points for which the fit on the data is displayed in panels (b)–(e). Residuals are shown below each panel.  $\text{CO}_2$  and  $\text{CO}$  lines are mostly located at energies respectively larger and smaller than  $2235 \text{ cm}^{-1}$ . Contributions to the fit corresponding to transitions of  $\nu_3$  or  $\nu_{\text{CO}}$  of  $0 \rightarrow 1$ ,  $1 \rightarrow 2$ , and  $2 \rightarrow 3$  are shown separately. Panel (f) shows a detail of panel (c).

transmittance, respectively.  $\sigma^2$  is the variance of the noise on the data, calculated from a wavenumber region without spectral activity. In short,  $\chi_{\text{red}}^2$  represents the normalized ratio of the variance of the residual of the fit to the variance of the



**Figure 6.** The reduced chi-squared for varying  $T_{rot}$ ,  $T_{1,2}$ ,  $T_3$ , and  $T_{CO}$  individually. The same time points are used as in figure 5. Time points are grouped in line style, while color indicates the tested temperature.

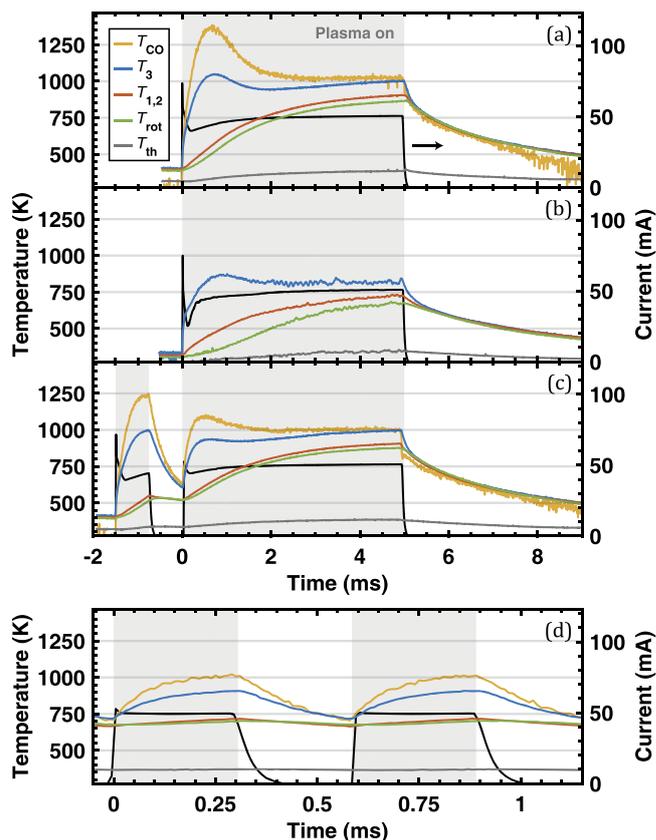
noise on the data. The closer  $\chi_{red}^2$  is to 1, the better the model fits the data, though  $\chi_{red}^2 < 1$  means that the model is overfitting.

In figure 6,  $\chi_{red}^2$  is plotted for parameter scans of  $T_{rot}$ ,  $T_{1,2}$ ,  $T_3$ , and  $T_{CO}$  for the time points of figures 5(b)–(e). The plots are constructed by fitting the data while fixing one of these temperatures at various values (horizontal axis) and calculating  $\chi_{red}^2$  of the resulting fit (vertical axis). In this way,  $\chi_{red}^2$  forms a shape with its minimum at the original fit outcome, generally in the shape of a parabola; a higher or lower temperature respectively results in too strong or too weak peaks for vibrationally excited species. However, at  $-0.15$  and  $7.00$  ms  $T_{CO}$  as well as  $T_3$  at  $-0.15$  ms show an asymmetric shape, leveling off at lower temperatures. At these temperatures, the densities of excited  $\nu_{CO}$  and  $\nu_3$  become so small, that the remaining transmittance peaks are not distinguishable from noise. In figure 5(a), this explains  $T_{CO}$  being fitted too low before the plasma pulse and after  $7.00$  ms.

Furthermore, the width of the parabola shape can be used as an indication for the sensitivity of the fitted transmittance to a particular parameter.  $T_{rot}$  and  $T_{1,2}$  show equally sharp shapes with an average half width at  $\chi_{red}^2 = \chi_{red,min}^2 + 0.5$  of 30 K and 27 K, respectively. The shapes of  $T_3$  are with a half width of 67 K twice as broad, while those of  $T_{CO}$  are by far widest at 357 K. A variation in the measured transmittance (e.g. resulting from a fluctuation in the plasma conditions of the emission background with respect to the normal transmission measurement, see section 2) is therefore likely to cause largest deviations in the fitted  $T_{CO}$ .

#### 4.3. Influence of initial gas mixtures

To further discuss the temperature development during the plasma cycle, the fitting results of different cycles are compared in figure 7, where panel (a) shows data from the same



**Figure 7.** Four time-resolved measurement series at a pressure of 6.7 mbar and plasma current of 50 mA. The plasma current and fitted temperatures are plotted versus time. (a) 5–10 ms on-off measurement, same as in figure 5. (b) Single-pulse measurement, in which the off-time is increased to 150 ms to remove most of the CO and O<sub>2</sub> before the next discharge. (c) 0.75–0.75–5–10 ms on-off-off measurement. The same as (a), but with a 0.75–0.75 ms on-off pre-pulse. (d) 0.3–0.3 ms on-off (two periods are shown).

experiment as figure 5(a). During this 5–10 ms on-off pulse, a molecule experiences on average ca. 150 discharges before leaving the reactor. The fitted conversion factor of  $\alpha = 0.18$  corresponds to a mixture of 75.2% CO<sub>2</sub>, 16.5% CO, and 8.3% O<sub>2</sub> (see equations (6) and (7)). In contrast to this, in panel (b) the fit outcome of a measurement is shown where a molecule sees only one plasma pulse. To achieve this, the flow rate is increased from 7.4 sccm to 166 sccm of CO<sub>2</sub> while the plasma-off time is increased to 150 ms. Now, the residence time of the gas of ca. 100 ms is well below the off time, purging the reactor of most CO and O<sub>2</sub> before the next discharge. Accordingly, this measurement is referred to as the single-pulse measurement. It should be noted that the conversion during a single discharge is not enough to be able to accurately fit  $\alpha$  or  $T_{CO}$ .

Practically, due to the longer plasma-off time, the measurement time increases from the regular two times 2 h (transmission and emission measurement) to two times 10 h, which makes it challenging to maintain constant discharge conditions and IR detector temperature. Further increasing the flow rate reduces the required off time and therefore the measurement time, but would also increase the renewal of the

gas during the discharge, which is already 5%. The injection of thermal gas in an ongoing discharge is likely to influence the temperature dynamics and should therefore be minimized.

Comparing the graphs in figures 7(a) and (b), the development of temperatures over time is similar: when the plasma turns on,  $T_3$  rapidly increases with a maximum around 0.7 ms, after which  $T_{\text{rot}}$  and  $T_{1,2}$  increase and all temperatures level off in a non-thermal equilibrium. The temperatures quickly thermalize after plasma-off, which takes somewhat longer in the single-pulse measurement. The difference in absolute values of the temperatures between (a) and (b) is to a large extent explained by the lower initial temperatures, resulting from a full renewal with cold gas before the next pulse. Furthermore, during the single pulse the temperatures show irregularities, best visible between 2 and 5 ms, which result from variations between single discharges. When the plasma-off time is small, discharges ignite more stable. Other differences, such as the increased  $T_{1,2}$  between 0 and 2 ms, are attributed to the absence of interactions of  $\text{CO}_2$  with  $\text{CO}$  or  $\text{O}_2$ , this being the prominent difference between the plasma conditions.

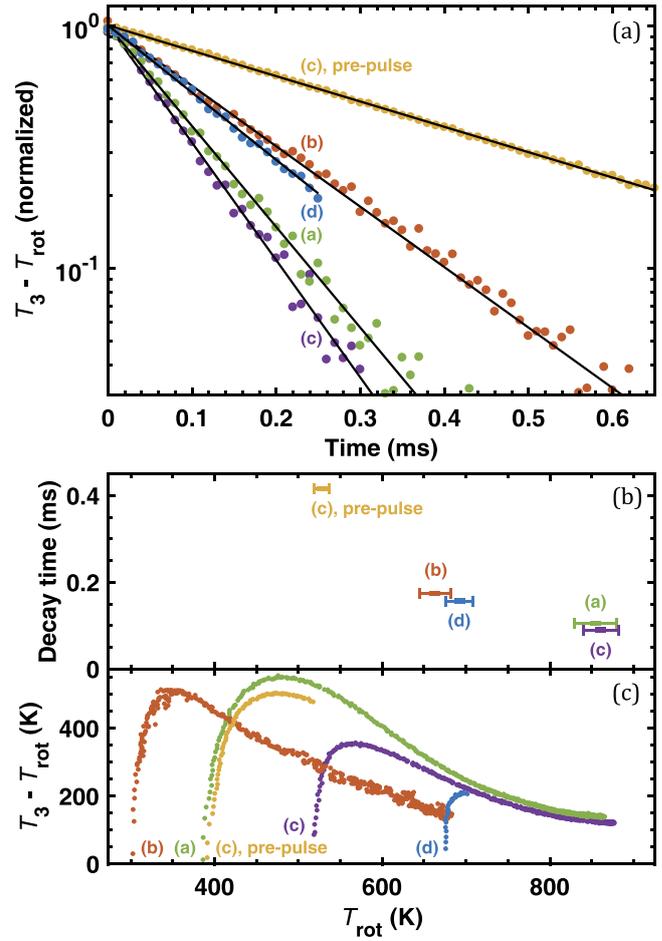
#### 4.4. Excitation of the asymmetric stretch mode

Focussing on the excitation of the asymmetric stretch vibration of  $\text{CO}_2$ , potentially relevant for an efficient dissociation, it is examined whether an elevated  $T_3$  is typical for the start of a discharge. To do so, figure 7(c) shows the result of a measurement where the 5–10 ms on–off pulse is preceded by a 0.75–0.75 ms on–off pre-pulse. The temperature development during the pre-pulse matches the first 0.75 ms in the pulse of panel (a). At the start of the 5 ms pulse,  $T_3$  peaks again, but reaches a lower maximum. The pulse continues comparable to the one in panel (a). After the pre-pulse, the relaxation of  $T_3$  to  $T_{\text{rot}}$  takes longer than at the end of the 5 ms plasma pulse and when after 0.75 ms the 5 ms pulse starts,  $T_3$  is not fully relaxed yet.

Based on this, it is examined whether a repeating rapid excitation with an incomplete relaxation can lead to further elevation of  $T_3$ . To this purpose, the results of an on–off cycle of 0.3–0.3 ms is shown in figure 7(d). From the graph, it can be seen that  $T_3$  never completely relaxes, but its maximum excitation is not higher than for the other cycles. Besides,  $T_{\text{rot}}$  and  $T_{1,2}$  stay relatively high and constant between 650 and 725 K.  $T_3$  relaxation after the pulse takes place with a similar speed as for the single pulse in panel (b).

To quantify the relaxation of  $T_3$  to  $T_{\text{rot}}$  for all panels of figure 7, the difference between these two temperatures after plasma off is fitted with a single exponential decay. The relaxation after the pre-pulse in panel (c) is fitted as well. The results are shown on a logarithmic scale and normalized to the initial temperature difference in figure 8(a). The labels of the data correspond to the panels of figure 7. The fitted exponential curves are presented as solid black lines and are in good agreement with the data.

The different slopes show that the characteristic decay time varies strongly between data sets. While most experimental conditions during these plasma-off phases are similar,



**Figure 8.** (a) Normalized relaxation of  $T_3$  to  $T_{\text{rot}}$  versus time after plasma off. The labels correspond to the panel labels of figure 7. The black solid lines represent the fitted exponential decay. (b) The characteristic decay times versus the rotational temperature during relaxation. (c) The elevation of  $T_3$  with respect to  $T_{\text{rot}}$  versus the rotational temperature, during the plasma-on phases of figure 7.

the rotational or translational temperature ranges from 530 K during the pre-pulse relaxation (c) to 860 K during the relaxation of (a) and (c). Figure 8(b) shows the fitted characteristic times versus the rotational temperature during the relaxation. Since  $T_{\text{rot}}$  varies over time, the decay time is plotted versus the average rotational temperature during a time period of twice the fitted characteristic decay time. The horizontal error bars represent twice the standard deviation of  $T_{\text{rot}}$  over this same period. The graph indicates a strong decrease of the decay time with increasing rotational temperature. This agrees with increasing rate constants for  $\nu_3$  relaxation with increasing translational temperature [43, 44].

The rotational temperature dependence of  $T_3$  relaxation to  $T_{\text{rot}}$  should be apparent in the plasma-on phase as well. To illustrate this, panel (c) of figure 8 shows  $T_3 - T_{\text{rot}}$  during the discharges of figure 7 versus the rotational temperature. All graphs develop similarly towards an equilibrium between relaxation and excitation, e.g. by electron impact, starting with a rapid increase at low  $T_{\text{rot}}$  when the discharge ignites. After reaching equilibrium around the maximum, the

equilibrium temperature gradually decreases with increasing  $T_{\text{rot}}$ . The rotational temperature dependence of this decrease is proportional to the one of the  $T_3$  to  $T_{\text{rot}}$  decay time in figure 8(b). This illustrates the influence of translational temperature dependent relaxation on the  $T_3$  elevation during a discharge.

The fact that the single-pulse measurement (b) shows the same development, but does not align with the rest, can be explained by the absence of CO for the single pulse versus a fitted 16.5%, 17.7%, and 22.0% of CO for (a), (c), and (d), respectively. It is known from literature that CO can stimulate vibrational excitation of the asymmetric stretch mode of  $\text{CO}_2$  [13]. Hence, the substantial concentration of CO in pulses (a), (c), and (d) results in a higher equilibrium temperature for  $T_3$ .

On the other hand, this effect should limit the excitation of  $T_{\text{CO}}$ , which becomes apparent with a comparison to the modeling work of Gorse and Capitelli [45]. Their self-consistent and time dependent model of a DC discharge, starting in pure CO, is run at very similar conditions, at a pressure of 6.7 mbar, a fixed translational temperature of 500 K, a reduced electric field of 60 Td, and an electron density of  $10^{10} \text{ cm}^{-3}$ .

The modeling results show an initial increase of  $T_{\text{CO}}$ , which stops and slowly reverses when at 7 ms enough deactivating species like  $\text{CO}_2$  are formed. The effect of  $\text{CO}_2$  on the vibrational temperature of CO is well visible when comparing concentrations and temperatures. With up to a few percent of  $\text{CO}_2$  in the model of [45],  $T_{\text{CO}}$  can reach 3500 K, while with 75% of  $\text{CO}_2$  in figure 7(a) of the current work, at  $T_{\text{rot}} = 500 \text{ K}$ ,  $T_{\text{CO}}$  does not exceed 1350 K.

## 5. Conclusions

We have demonstrated a method to determine elevated vibrational temperatures of  $\text{CO}_2$  and CO in a glow discharge in a time-resolved way, using *in situ* Fourier transform infrared spectroscopy. An algorithm is developed to analyze the measured transmittance spectra. As the outer ends of the reactor are filled with gas at a temperature colder than the gas in the discharge, a thermal-volume fraction is introduced in the model. The algorithm has been used to fit a previously published  $\text{CO}_2$  spectrum, showing highly vibrationally excited  $\text{CO}_2$  transitions. There is a very good agreement between fit and data.

To study the influence of the initial gas mixture, a measurement where the gas residence time is much longer than the plasma period is compared to one where the gas is fully renewed between two pulses. Both show a qualitatively similar development of temperatures over time. Absolute differences are attributed to the significantly increased presence of CO and  $\text{O}_2$  in the multiple-pulse measurement in regard to the single-pulse measurement. Due to the shorter plasma-off time of the multiple-pulse measurement, the discharge ignites in a more stable and consistent way.

It is experimentally shown that the temperature dependence of  $T_3$  relaxation is likely to be the leading mechanism for the decrease of  $T_3$  elevation with increasing  $T_{\text{rot}}$ . The  $T_3$  peak found at the start of a sufficiently long plasma pulse is therefore not so much a consequence of a starting discharge, but is caused by a low  $T_{\text{rot}}$ . Hence, to gain higher excitations of the asymmetric stretch mode, potentially relevant for the efficient dissociation of  $\text{CO}_2$ , relaxation could be strongly impeded by keeping the gas temperature low. In this regard, this study will be continued with measurements on a reactor in which the gas temperature can be manipulated by circulating a temperature controlled liquid trough a double reactor wall.

## Acknowledgments

This work is partially funded by the Netherlands Organisation for Scientific Research (NWO), under reference 713.013.003, and partially by LABEX Plas@par receiving financial aid managed by the French National Research Agency (ANR) under the references ANR-11-IDEX-0004-0, and ANR-16-CE06-0005.

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