Mode resolved heating dynamics in pulsed microwave CO$_2$ plasma from laser Raman scattering

Citation for published version (APA):

Document license:
TAVERNE

DOI:
10.1088/1361-6463/ab5311

Document status and date:
Published: 30/01/2020

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.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the “Taverne” license above, please follow below link for the End User Agreement:
www.tue.nl/taverne

Take down policy
If you believe that this document breaches copyright please contact us at:
openaccess@tue.nl
providing details and we will investigate your claim.
Mode resolved heating dynamics in pulsed microwave CO\textsubscript{2} plasma from laser Raman scattering

To cite this article: D C M van den Bekerom et al 2020 J. Phys. D: Appl. Phys. 53 054002
Mode resolved heating dynamics in pulsed microwave CO$_2$ plasma from laser Raman scattering

D C M van den Bekerom©, A van de Steeg©, M C M van de Sanden and G J van Rooij©

Dutch Institute for Fundamental Energy Research, Eindhoven, The Netherlands
E-mail: g.j.vanrooij@differ.nl

Received 17 June 2019, revised 16 October 2019
Accepted for publication 31 October 2019
Published 22 November 2019

Abstract
Efficient CO$_2$ reduction is predicted for CO$_2$ microwave plasma by virtue of predominant excitation of the asymmetric stretch vibration. Although interpretation of ongoing research is generally based on this mechanism, direct measurement of the power partitioning to support the assumed preferential vibrational excitation in CO$_2$ microwave plasma is currently lacking. Here, such measurements are performed on a 100 $\mu$s pulsed microwave CO$_2$ discharge. The <1% duty cycle ensures low gas temperature conditions at the discharge onset. Raman and Rayleigh scattering are employed to reveal vibrational, rotational, and gas temperatures in a spatially and temporally resolved manner. A novelty in the approach is that asymmetric stretch excitation is determined from the bending—symmetric stretch Raman spectrum. During the first 40 $\mu$s a significant inter-vibrational non-equilibrium is observed with the symmetric stretch and bending temperature reaching 750 K and the asymmetric stretch temperature reaching 1150 K. A maximum rotational-vibrational non-equilibrium occurs after 60 $\mu$s when the rotational temperature is half of the 1150 K vibrational temperature. Rotational and translational modes are measured to be in equilibrium at all times. The power partitioning is analyzed to estimate the power consumed by vibrational excitation, which is used to estimate the reduced electric field in the discharge. This work confirms strong vibrational excitation in CO$_2$ microwave plasma albeit less predominant than often assumed.

Keywords: microwave plasma, CO$_2$ reuse, vibrational excitation, Raman scattering, microsecond pulsing

(Some figures may appear in colour only in the online journal)
reaction coordinate of one oxygen atom separating to form a CO molecule, which corresponds to the lowest dissociation energy. This is opposed to the bending mode that would split off an oxygen molecule, and the symmetric stretch that would split off two oxygen atoms. Moreover, the asymmetric stretch quanta are largest, therefore difficult to convert via collisions into kinetic energy, and hence best suited to exhibit a strong non-equilibrium.

The efficient vibrational pumping in CO2 leads to a situation in which higher vibrational modes are much more populated than they would be in a thermal equilibrium, ultimately producing the so-called Treanor distribution [5]. The condition for achieving overpopulation of the higher vibrational levels is that the vibration–vibration (V–V) relaxation rates are much higher than vibration–translation (V–T) relaxation rates. This is the case for the asymmetric stretch mode of CO2 provided that the gas temperature remains low. The V–V relaxation rates decrease with increasing gas temperature, while the V–T rates increase, so that high gas temperatures will quench any overpopulation of higher vibrational levels. The level of overpopulation of high vibrational levels determines the efficacy of vibrational excitation for CO2 dissociation [6].

Faced with a resurgence of interest in CO2 utilization due to climate change, a number of groups is investigating the maximally achievable energy efficiency for reduction of CO2 in plasma [7]. So far none of these efforts have come close to the reported 90% energy efficiency. Among the highest efficiencies that were measured in recent years is the value of 50% as was reported by our group [2, 8]. However, in that work the gas temperatures were estimated on the basis of Rayleigh scattering to be in excess of 3500 K in the core, which seems to be incompatible with a strong vibrational non-equilibrium. Such high temperatures suggest that thermal equilibrium conversion is significantly contributing to the conversion.

We followed this work up by measuring the temporally and spatially resolved temperature while pulsing the power in the kHz range [9]. The temperature evolution was studied in scans of the duty cycle allowing to vary the power density without changing the mean power. The energy efficiency was found to increase with power density due to higher central gas temperatures that favor local chemistry above radial and advective power losses.

In this paper we aim to depart from the thermal conversion regime to the true strongly non-equilibrium regime that is generally assumed to exist in microwave CO2 discharges. The dynamics of gas heating are studied to assess the natural limitations to promoting non-equilibrium effects. The general concept is to start from room temperature by power pulsing at low duty cycles and to measure the gas heating rates while resolving the different degrees of freedom. The low gas temperature suppresses vibration–translation (VT)-relaxation, reducing loss of vibrational excitation. The expectation is that as the gas temperature increases, quenching of vibrational excitation will set in, increase the gas heating rate, and thermalize the system.

Strong vibrational non-equilibrium has been shown in plasmas of diatomic molecules like H2 [10–13], N2 [14–17] and CO [18]. A vibrational non-equilibrium may be expected to be more difficult to sustain in CO2 because of the low energy bending vibration that can rapidly exchange energy with translation (VT-relaxation) and quench vibrational excitation. Vibrational nonequilibrium in pure CO2 has so far only been directly measured in low power glow discharges [19–22].

A range of diagnostics has been used in the past for measuring vibrational temperatures in CO2. For example, alkaline impurities were added to the discharge to estimate the vibrational temperature indirectly [21, 23]. Their temperature was assessed from the Doppler broadening in their line emission and assumed to be in thermal equilibrium with the vibrational excitation of the CO2 inventory. More direct methods that were applied in glow discharges include tunable diode laser absorption spectroscopy (TDLAS) [19, 22] and Fourier transform infrared absorption spectroscopy (FTIR-AS) [20], or gain measurements [21] (in CO2 lasers). These are line-of-sight integrated measurements and are therefore not optimal with the significant temperature gradients that have been encountered in microwave plasma [2]. Vibrational analysis of C2 swan band optical emission was used as proxy for the overall vibrational temperature measurements [24]. However, this requires a justification that the vibrational temperature of the electronically excited product can be assumed to be in vibrational equilibrium with the electronic ground state of the reactant, which is generally not evident.

The present paper overcomes the problems of path integration and indirect information by employing laser scattering, which provides spatial as well as temporal resolution. The scattered light originates from the well-defined intersection of the focused laser beam and the collection optics during the duration of the laser pulse. The vibrational and rotational spectra of the polyatomic CO2 molecule are well understood by virtue of the high molecular symmetry [5]. It allows an analysis revealing the heating dynamics of the neutral CO2 inventory in microwave plasma whilst resolving the different degrees of freedom in the CO2 molecule. A novelty in the approach is the discrimination between asymmetric stretch versus symmetric stretch and bending vibration by analysis of the symmetric stretch vibrational Raman spectrum. The required methodology was developed as part of this work and the experimental results represent the first direct proof of the existence of a vibration–vibration non-equilibrium in a pure CO2 microwave plasma. The vibrational temperature measurements are supplemented by rotational and gas temperature measurements. The evolution of the temperatures of the different degrees of freedom is assessed by evaluation of the power partitioning over the different modes of freedom.

2. Interpretation of the CO2 vibrational Raman spectrum

The CO2 molecule has 3N − 5 = 4 vibrational normal modes: the ν1 symmetric stretch, the doubly degenerate ν2 bending, and the ν3 asymmetric stretch. The symmetric stretch is the only Raman active fundamental vibration. It is in Fermi-resonance with the overtone of the bending mode. In this section it is shown how population of higher asymmetric stretch
levels can be inferred from the Fermi dyad between 1200 and 1500 cm$^{-1}$. The approach is similar to determination of all vibrational populations from the IR-absorption bands of the asymmetric stretch mode [20]. For example, the Raman transition $(0 0 0 1) \rightarrow (1 0 0 1)$ will be proportional to the density in the $(0 0 0 1)$ vibrational state (the first excited asymmetric stretch level). Due to the Fermi-splitting, the vibrational spectrum consists of two branches; a high energy branch with the ground state peak at 1388 cm$^{-1}$, and a low energy branch with the ground state peak at 1000 cm$^{-1}$.

A simulated CO$_2$ vibrational Raman spectrum is shown in figure 1 to illustrate how $\nu 3$ excitation comes about in the spectrum. The behavior of the Raman shifts in dependence of the vibrational excitation is rooted in the anharmonicity of the modes. In the high energy branch, the $\nu 1$ and $\nu 2$ modes have a positive anharmonicity, i.e., the level spacing and thus the Raman shift increases for higher levels. Oppositely, $\nu 3$ vibrational level spacing decreases for higher vibrational quantum. Consequently, the lowest energy peaks that correspond to higher asymmetric stretch levels are well separated from higher $\nu 1$ and $\nu 2$ levels. Conversely, in the lower energy branch all higher vibrational levels shift to lower energy and peak congestion occurs. The higher energy branch (1388 cm$^{-1}$) therefore offers an opportunity to quantify $\nu 3$ population.

In fact, the intensity of the single $(0 0 0 1) \rightarrow (1 0 0 1)$ transition at 1365.4 cm$^{-1}$ will be used to quantify $T_v$. Higher asymmetric stretch levels can be disregarded in view of insignificant population given the large energy of the asymmetric stretch fundamental of 2349 cm$^{-1}$ compared to a typical vibrational temperature of below 10000 K. Even the population of the transition at 1365.4 cm$^{-1}$ belonging to the first asymmetric level will be relatively low at the expected vibrational temperatures.

In close proximity to the transition of interest at 1365.4 cm$^{-1}$ is another line that belongs to the $(0 0 0 0) \rightarrow (1 0 0 0)$ transition of the $^{13}$C$^{16}$O$_2$ isotopologue and is positioned at 1370.1 cm$^{-1}$. Due to the limited spectral resolution, these two lines appear to be overlapping. The $^{13}$C$^{16}$O$_2$ line at 1370.1 cm$^{-1}$ is usually not of interest, but because it overlaps with the 1365.4 cm$^{-1}$ line it must be included in the synthetic spectrum in order prevent overfitting of the line of interest at 1365.4 cm$^{-1}$, which would otherwise lead to an overestimation of $T_v$. At higher temperatures the intensity of the $(0 0 0 0) \rightarrow (1 0 0 0)$ line of the $^{13}$C$^{16}$O$_2$ isotopologue is greatly reduced due to a drop in the relative population of the ground vibrational state in favor of higher vibrationally excited states. Though the interference of the 1370.1 cm$^{-1}$ line at higher temperatures is limited due to its low intensity, the line is included in the spectral fit in all cases.

The relative cross sections for both isotopologues were calculated according to the method described in [25] whilst including the bending mode overtones as in [26]. A detailed procedure for calculating the cross sections and synthetic spectra can be found in the appendix. The spectral constants were taken from [28] and the absolute cross sections for the main isotopologue were taken from [26]. The absolute cross sections for $^{13}$C$^{16}$O$_2$ were obtained by fitting the spectral model to a measured spectrum at room temperature. The fitted cross-sections did not deviate significantly from those of the main isotopologue, which justifies the use of the literature values for both isotopologues.

The spectra were calculated taking vibrational levels up to 10000 cm$^{-1}$ into account for $^{13}$C$^{16}$O$_2$ and vibrational levels up to 5000 cm$^{-1}$ for $^{1}$C$^{16}$O$_2$. The vibrational spectra also depend on the rotational temperature due to a small variation in rotational constants of different vibrational levels. However, this dependence is too small to extract accurate rotational temperatures from the vibrational spectrum at the current spectral resolution. Instead, the rotational temperature is determined from the purely rotational spectrum and used as input to calculate the rotational broadening in the vibrational spectra.

The model for fitting the experimental spectra with two independent vibrational temperatures $T_{\nu 1,2}$ and $T_{\nu 3}$ follows from simply splitting the vibrational level energies in a symmetric part ($E_{\nu 1,2}$) and antisymmetric part ($E_{\nu 3}$) and ignoring mixed terms [20]:

\[ E_{\nu 1,2} = \frac{1}{2} \nu 1 \nu 2 + \text{constant} \]

\[ E_{\nu 3} = \nu 3 \]

where $\nu 1$ and $\nu 2$ are the frequencies of the asymmetric stretch and $\nu 3$ is the frequency of the symmetric stretch.
The meaningfulness of fitting two vibrational temperatures was checked by evaluation of the residue in comparison with fitting a single vibrational temperature. An experimental spectrum comparing a equilibrium and non-equilibrium fit is shown in figure 2. To determine the uncertainties in the fitted temperatures, the measured spectrum was first fitted with a non-equilibrium fit and RMS of the residue was determined. Then $T_{v1,v2}$ and $T_{v3}$ were varied separately until the RMS of the residue was twice that of the least-squares fit. This resulted in temperature differences of $\Delta T_{v1,v2} = 30$ K and $\Delta T_{v3} = 92$ K, corresponding to an error of 5% for $T_{v1,v2}$ and 9% for $T_{v3}$. A similar procedure resulted in an error of 12% for $T_{rot}$. This error is relatively high because individual rotational lines are not resolved, but rather the envelope of the spectrum is fitted. The gas temperature likely has a relatively large systematic error as well, because it was measured by Rayleigh scattering which is sensitive to background reflections and gas composition. For determining the uncertainty we assume that rotational and gas temperature rapidly equilibrate, and compare the gas and rotational temperature measured by Rayleigh and Raman scattering respectively, resulting in an error in $T_{gas}$ of about 15%.

3. Experimental

The experimental layout is schematically depicted in figure 3. A 27 mm inner diameter quartz tube is inserted through the rectangular waveguide. Pure CO$_2$ is tangentially injected into the tube.
at a flow rate of 4 slm. The cell pressure is set to 25 mbar, which is the maximum pressure at which the pulsed plasma was found to ignite reliably. A solid-state amplifier (2.45 GHz, up to 600 W peak power) produces microwave pulses of 100 µs duration at a repetition rate of 30 Hz. The 30 Hz results in three plasma pulses per laser pulse (10 Hz), which seems unnecessary but was chosen as it improved plasma ignition reliability. Forward and reflected power are measured with DM211P microwave diodes connected to a 50 dB directional coupler. A three-stub tuner is included to tune the microwave cavity.

Laser scattering is conducted similarly with the frequency doubled output of a Nd:YAG laser (6 W, 10 Hz). The laser beam is focused in the center of the plasma, which is typically few mm different from the center of the flow tube. Scattered light is collected and imaged onto an array of 40 fibers with two 100 mm achromatic doublets so that an axial range of ~13 mm is covered. The fibers relay the light to the custom-built Littrow spectrometer (150 mm diameter lens, 100 × 100 mm 1180 ll mm⁻¹ grating, 0.85 mm mm⁻¹ linear dispersion). An ICCD camera is gated to the laser pulse (20 ns gate time) to minimize plasma light background in the spectra. The temperature measurements are resolved in time by scanning the delay time of the laser pulse with respect to the plasma pulse. The number of accumulations depends on the signal intensity and is typically 200 for Rayleigh, 2400 for rotational Raman, and 6000–9000 for vibrational Raman. Spectra are plasma light as well as straylight corrected.

The spectrometer uses no additional slit in order to maximize throughput. Hence, the fiber determines the instrument function, which was found to fit best the convolution of a Gaussian, Lorentzian and elliptical function as line shape function. The broadening constant for each of these components was first fitted to the Rayleigh peak and subsequently optimized in the vibrational Raman spectrum to minimize the residue. The FWHM of the resulting instrumental line shape is 7 cm⁻¹.

Gas kinetic temperatures are calculated from the neutral density obtained from Rayleigh scattering, assuming 300 K at the discharge onset and constant pressure over the discharge pulse, and neglecting product formation (which affects the effective Rayleigh cross section [2]). Rotational Raman spectra are recorded with a linear polarizer in the optical path to block most of the Rayleigh light. The Stokes branch is completely visible even at high rotational temperatures (1500 K). The rotational temperature is measured by fitting the spectral shape. Vibrational Raman spectra are recorded over a spectral window of typically 1500 cm⁻¹ of the Stokes branch. A long pass filter is placed (instead of the polarizer) in the optical path to remove stray light. Spectra of the 40 fibers are binned together to improve the signal to noise ratio. Only the transitions to the highest levels of the Fermi resonant levels (1388 to 1500 cm⁻¹) are fitted because of the presence of a distinct ν3 band.

The evolution of the discharge shape and size is recorded by placing the spectrometer’s ICCD camera at the position of the fiber array entrance so that all spontaneously emitted plasma light is collected. Again, the ICCD gating is scanned with respect to the plasma pulse to yield the temporal evolution.

4. Results

Tuning of the microwave cavity to the impedance of the plasma pulses is not trivial. Whereas in continuous operation zero reflection can usually be realized, the continuously changing impedance of the developing discharge in pulsed operation makes that zero reflection can only be obtained for a particular phase of the discharge. In order to realize reliable ignition, the moment of minimal reflection was chosen just after ignition. This resulted in the absorbed power evolution that is seen in figure 4. The forward power is a square pulse with a peak power of 600 W. The reflected power drops to zero between 2 and 7 µs, remained zero until roughly 20 µs, and finally increased towards the end of the pulse. The temperature evolutions that are to follow below must be viewed in relation to this strong variation in effective power deposited to the plasma.

On the right of the graph, a series of plasma light images is shown that reflects the spherical shape at ignition at point a, growth/elongation during phase (a)–(c), the contraction during phase (c) and (d), and intensification during phase (d) and (e) of the discharge. The integrated intensity of these images (and intermediate ones not shown here) is also plotted in the graph. From the moment the plasma was ignited, the plasma emission intensity increased for 60 µs (phase (a)–(e)). A remarkable feature is that the discharge continued to develop after the point that the power coupling started to deteriorate, (phase (c)–(e)). It is the phase in which the discharge contracted. After point e, the light emission decreased, which must be due to either changing plasma conditions (decreasing electron density and/or temperature) or neutral gas density (due to increasing gas temperature given the constant reactor pressure). Given the dynamic behavior of all parameters of the discharge, it will not be possible to conclude the exact mechanism here without further knowledge of e.g. the electron density and temperature and/or the reduced electric field, aspects that are beyond the scope of the present work.

We note that continuous discharges also exhibited contraction, which was mostly determined by pressure and power. However, particularly pressure was significantly higher than under the contraction conditions here: >120 mbar for the same input power [2]. This difference is easily explained by the high temperatures of 3000–4000 K measured under these conditions compared to the much lower temperature regime that we entered in this work by virtue of the low duty cycle pulsing.

Having established the dynamic behavior in terms of power input (due to impedance variation) and power density (due to discharge contraction), we assess the time evolutions of vibrational, rotational, and gas temperatures that were measured in the center of the plasma, as shown in figure 5. It is observed that Tν3 increased fastest, to about 1000 K. The spectrum was not sensitive to Tν3 during the first few µs, when the (00’1) vibrational level was still too faint to be resolved from the ground state isotopologue. The response of Tν1ν2 was slower and reached 1000 K after 40 µs. From this moment on, a more or less stable non-equilibrium of 500 K temperature difference was sustained between Tν1ν2 and Tν3 with a
After 60 µs, the sensitivity to the asymmetric stretch feature in the Raman spectrum became too poor for fitting $T_{\nu_3}$ independently. It is assumed that all vibrational modes equilibrated, which seems a reasonable assumption as the temperature curves already indicate convergence. After equilibration of the vibrational modes, the vibrational temperature remained significantly higher than the rotational and gas temperature, and a nonequilibrium of 600 K was sustained. Vibrational and rotational temperatures were not in equilibrium during the entirety of the 100 µs pulse, while rotational and gas temperature were always in equilibrium.

The Raman spectrum was also evaluated for the appearance of reaction products. The 1900–2200 cm$^{-1}$ range was
Figure 6. Translational, rotational, and vibrational heat capacities as a function of temperature. The contribution of expansion work is included in $C_p^{m,\text{gas}}$. At low temperatures, vibrational levels are not excited and hence have zero heat capacity. The slower convergence of $C_p^{m,\text{vib,1}}$ compared to $C_p^{m,\text{vib,3}}$ is due to its much higher vibrational energy $\hbar \omega_{1,3}$.

inspected for the vibrational Raman spectrum of CO, and the 1250–1550 cm$^{-1}$ range (partly overlapping with the CO$_2$ vibrational spectrum) for O$_2$ [29]. As no spectral features were observed in these spectral ranges, we conclude that CO$_2$ dissociation was not significant in view of a power balance as will follow below.

5. Interpretation and discussion

Having measured the heating dynamics in a CO$_2$ microwave plasma discharge, we wish to analyze the power partitioning in the discharge to obtain insight in the mechanism that causes the observed gas heating rate. After all, the gas heating determines the quenching rate of vibrational excitation and must be controlled in order to enhance non-equilibrium effects dominating the CO$_2$ chemistry.

The power partitioning over all degrees of freedom, explicitly distinguishing between the translation, rotation, and vibration, is found by relating a small change in the molar enthalpy $dH^m$ to a change in the temperature of all of the four degrees of freedom:

$$dH^m = C_{p,\text{gas}}^m dT_{\text{gas}} + C_{p,\text{rot}}^m dT_{\text{rot}} + C_{p,\text{vib,1,2}}^m dT_{\text{vib,1,2}} + C_{p,\text{vib,3}}^m dT_{\text{vib,3}}.$$  \hspace{1cm} (2)

The heat capacities at constant volume $C_V^m$ for translations and rotations are given by the equipartition theorem, while heat capacity for vibrations can be derived from the partition function that is known for vibrational modes. The difference between the heat capacity at constant volume $C_V^m$ and the heat capacity at constant pressure $C_p^m$ is the contribution of the work due to expansion, $pdV$, which is zero for changes in temperature of rotation and vibration. This results in the relation $C_p^{m,\text{gas}} = C_V^{m,\text{gas}} + R$ for translations, while for rotations and vibrations $C_p = C_V$. Hence, we find the following expressions for the heat capacities:

$$C_{p,\text{gas}}^m = \frac{5}{2} R$$  \hspace{1cm} (3)

$$C_{p,\text{rot}}^m = R$$  \hspace{1cm} (4)

$$C_{p,\text{vib},i}^m = d_{i,i} z_i \left( \ln z_i \right)^2 R.$$  \hspace{1cm} (5)

Here, $i$ denotes the vibrational normal mode ($i = 1, 2, 3$), $d_{i,i}$ the degeneracy and $z_i$ the Boltzmann factor:

$$z_i = \exp \left( -\frac{\hbar \omega_{i,i}}{kT_{\text{vib},i}} \right).$$  \hspace{1cm} (6)

Here, $\omega_{i,i}$ is the energy of the fundamental vibration, and $T_{\text{vib},i}$ the vibrational temperature. We note that in the high temperature limit ($kT_{\text{vib},i} \gg \hbar \omega_{i,i}$) vibrations contribute a total of $2 \cdot \frac{1}{2} R$ per normal mode due to their kinetic and potential energy contributions. The heat capacities calculated with equations (3)–(5) are plotted as a function of temperature in figure 6. It is seen that $C_{p,\text{vib,1,2}}^m$ is much larger than $C_{p,\text{vib,3}}^m$ towards lower temperatures due to two effects. Firstly, it is the sum of two modes of which the bending is doubly degenerate, so that it can reach the value of 3 R. Secondly, the vibrational energies of the symmetric stretch and bending mode are much lower than that of the asymmetric stretch and hence the vibrational levels become accessible at lower temperatures.

We find the input power partitioning over the different modes by multiplying the time derivative of the measured temperature traces with the corresponding heat capacity. The temperature evolutions in figure 5 were first interpolated at a regular horizontal spacing of 5 μs, which yielded the dashed lines in the figure. A 2nd-order Savitsky–Golay filter with a 7-point window was subsequently used to determine the time derivative of the temperatures. The power partitioning...
is shown in figure 7. The advantage of expressing the power partitioning in terms of power per molecule is that it can be directly determined from the temperatures traces. Doing so liberates us from making assumptions on the plasma volume, which may be tenuous in light of potentially non-overlapping profiles of power deposition, electron density, and reactive species.

The picture in terms of power partitioning is significantly different from the measured temperature evolutions. It shows that, although the temperature of the asymmetric stretch mode was rising fastest, most of the power was actually being deposited into the symmetric stretch and bending modes, right from the beginning of the pulse. It was the small heat capacity causing the asymmetric stretch temperature to increase so rapidly. The translational heating was starting to consume most of the input power from roughly half way the pulse.

The black dashed curve in figure 7 reflects the local total absorbed power per molecule. In order to compare the total power that goes into heavy particle heating with the absorbed power, we need to divide by the molar volume (which is determined by the reactor pressure and the measured gas) and multiply with the plasma volume. We can only estimate the plasma volume on basis of the emission images, which is a rough estimate and prone to large errors. When we do this for \( t = 40 \mu s \), we estimate a volume of \( 1 \times 10^{-2} \text{ m}^3 \) and yield a heavy particle heating power of 200 W. This is 35% of the absorbed power. It implies that 65% of the input power is dissipated by other mechanisms such as ionization and (dissociative) electron excitation.

The electron power transfer fraction is determined by the electron energy or reduced electric field in the discharge and is depicted for a range of electron power transfer channels in figure 8 [4]. Our purpose is to compare these with the relative power transfer fractions we have determined from our laser scattering measurements and evaluate if we can find a reduced electric field regime where these match, both as sanity check and to gain further insight in the discharge properties.

Let us first consider the phase in the discharge in which the asymmetric stretch heating is strongest, i.e. around \( t = 10 \mu s \). In this phase, only vibrational heating is significant and other modes will therefore be neglected. We estimate from figure 7 that around \( t = 10 \mu s \) the power deposited into symmetric stretch and bending is twice the amount received by asymmetric stretch vibration. To estimate the reduced electric field, we look in figure 8 for a similar ratio between the symmetric stretch and bending mode (yellow and green curves) and the asymmetric stretch (blue curve), which is found for reduced electric fields larger than \( 6 \times 10^{-16} \text{ V cm}^2 \). Because the ratio stays roughly the same for higher electric fields, the \( 6 \times 10^{-16} \text{ V cm}^2 \) should be considered as a lower bound for the reduced electric field.

Later in the discharge we estimated a total power fraction of 35% being consumed by vibrational excitation (\( t = 40 \mu s \)). From figure 8 we read that this should occur at an even higher reduced electric field of \( 1 \times 10^{-15} \text{ V cm}^2 \). At this field strength, still a third of the power should be spent on excitation of asymmetric stretch levels, which is much more than what was estimated in figure 7 on basis of the temperature measurements. Perhaps the assumed equilibrium between all vibrational modes when the measurement lost sensitivity to \( T_{\nu_3} \) is not correct and possibly a strong \( T_{\nu_1, \nu_2} - T_{\nu_3} \) remained. However, evidence is currently lacking to determine this conclusively.

These reduced electric field estimates are much higher than optimal for power deposition in the asymmetric stretch is optimal (which occurs at \( 2.3 \times 10^{-16} \text{ V cm}^2 \)). The high reduced electric field (or, equivalently, high electron temperature) can be attributed to the fact that beginning of the pulse must be strongly ionizing to replenish the electron density that has been lost by recombination and convection during the long inter pulse delay. The time scale at which the plasma impedance was changing, evidenced by the changing power reflection, suggests ionizing conditions for a large part of the discharge pulse.
that time direct experimental evidence is presented demonstrating s. In effect, for the first µ
The vibrational-rotational non-equilibrium was maintained for the top sectors.

This research received funding from the Netherlands Organisation for Scientific Research (NWO) in the framework of the CO2 Neutral Fuels programme and the ENW PPP Fund for the top sectors.

Figure 8. Fractional electron power transfer in CO2 as a function of reduced electric field for different transfer mechanisms after [4].

6. Conclusions

It was demonstrated that vibrational Raman is a viable diagnostic to determine the vibrational non-equilibrium in CO2 plasma. Supplemented by rotational Raman and Rayleigh scattering, all relevant heavy particle temperatures in the non-equilibrium discharge could be diagnosed with high temporal (in principle down to the 10 ns laser pulse duration) and spatial resolution (0.3 mm is achievable on basis of the fiber diameter and collection optics magnification, in practice data binning was applied reducing the resolution to ~1 cm) using a single experimental scheme.

In the current configuration we demonstrated a T1,2 − T3 non-equilibrium of up to 500 K that was maintained for 40 µs. The vibrational-rotational non-equilibrium was maintained for the entire pulse duration of 100 µs. In effect, for the first time direct experimental evidence is presented demonstrating that a T1,2 − T3 non-equilibrium can be achieved in a pure CO2 microwave plasma by modulating the microwave power.

It was shown that although T3 is significantly larger than T1,2 during the onset of the pulse, the fraction of power deposited in the asymmetric stretch was much lower than the power in the symmetric stretch and bending mode due to its much lower heat capacity. The fraction of power deposited in vibrations was used to estimate the reduced electric field to be at least 6−10 × 10−16 V cm2, which is much too high for optimal power transfer to the asymmetric stretch mode and possibly a consequence of the strongly ionizing nature of the onset of the discharge. We therefore conclude that this work presents confirmation of strong vibrational excitation in CO2 microwave plasma albeit less predominant than often assumed.

Acknowledgments

This research received funding from the Netherlands Organisation for Scientific Research (NWO) in the framework of the CO2 Neutral Fuels programme and the ENW PPP Fund for the top sectors.

Appendix. Calculation of cross-sections and synthetic spectra

To calculate the vibrational Raman spectrum, the cross section for vibrational transitions within the spectral window were calculated. The CO2 molecule has 3N − 5 = 4 vibrational modes, and the vibrational state is hence described by four vibrational quantum numbers: v1, v2, ℓ, and v3. Because of the existence of an (accidental) Fermi-resonance, vibrational levels are strongly coupled if they have the same v1, ℓ, and m, where m is given by:

\[ m = v_1 + \left( \frac{v_2 - \ell + 1}{2} \right) . \]  

(A.1)

Levels for which these numbers are identical cannot be described accurately by quantum numbers v1 and v2 anymore. Instead, the vibrational state is described by quantum numbers m and r, where m is the number of mixed levels and r is the index of the Fermi-resonant level. We remark that notation may vary slightly between authors and the same variable can have different meanings, causing expressions to look different. Here we will follow the conventions of [25].

When m = 1, the vibrational level is not coupled and its energy can be directly calculated by:

\[ W^0 (v_1, v_2, v_3) = \sum_i \omega_i v_i + \sum_{ij} x_{ij} v_i v_j + g_{22} \ell^2 + \sum_{ijk} y_{ijk} v_i v_j v_k . \]  

(A.2)

When m > 1, the energy of the mixed levels can be found by diagonalizing the \( m \times m \) perturbation Hamiltonian \( H \):

\[ H = \begin{pmatrix} W^0_{11} & W^0_{12} & 0 & \cdots & 0 & 0 \\ W^0_{21} & W^0_{22} & W^0_{23} & \cdots & 0 & 0 \\ 0 & W^0_{31} & W^0_{32} & \cdots & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & 0 & \cdots & W^0_{m-1,m} & W^0_{m-1,m} \\ 0 & 0 & 0 & \cdots & W^0_{m-1,m} & W^0_m \end{pmatrix} . \]  

(A.3)

The matrix of the perturbation Hamiltonian \( H \) is a symmetric tridiagonal matrix with the diagonal elements given by the
unperturbed energy $W^0$. The matrix element $H_{ji}$ is thus the energy of unperturbed level $(v_1, v_2, v_3)$ with:

$$v_1 = m - i, \quad v_2 = \ell + 2(i - 1),$$

and $i = 1, 2, \ldots m$. The off-diagonal elements $H_{j+1,i} = H_{i,j+1}$ are given by:

$$W = (W_0 - \lambda_1 v_1 - \lambda_2 v_2 - \lambda_3 \ell - \lambda_3 v_3) \frac{1}{2} \sqrt{v_1 \left[(v_2 + 2)^2 - \ell^2\right]},$$

with $i = 1, 2, \ldots, m - 1$. Diagonalizing the Hamiltonian results in $m$ eigenvalues $E_r (r = 1, 2, \ldots, m)$ which are the energies of the perturbed levels $(m - 1, \ell, v_3)$. The perturbed state is a linear combination of the unperturbed states, with the eigenvectors $a_i$ corresponding to eigenvalues $E_r$, quantifying how much the unperturbed level contributes to the perturbed level $r$. For example:

$$(2 \ell^0 1)_1 = a_{11}(2 \ell^0 1) + a_{12}(1 \ell^0 1) + a_{13}(0 \ell^0 1).$$

The energies and eigenvectors were calculated for energies up to 10 000 cm$^{-1}$ for the main isotopologue, and up to 5000 cm$^{-1}$ for the $^{13}$CO$_2$ isotopologue. Line positions and intensities are calculated for every transition for which $\Delta m = 1, \Delta \ell = 0$, and $\Delta v_3 = 0$, that is, for every transition in the observed band.

Like for diatomic molecules, the cross-sections for any transition can be related to the cross section of the transition to the first excited vibrational levels. For a transition between two unperturbed levels, the cross section is given by [26]:

$$\langle \alpha \rangle = \left\{ \begin{array}{ll}
(\alpha_1)^0 \sqrt{v_1 + 1}, & \text{if } \Delta v_1 = 1 \\
(\alpha_2)^0 \sqrt{(v_2 + 2)^2 - \ell^2}, & \text{if } \Delta v_2 = 2
\end{array} \right.$$

(A.6)

where $(\alpha_1)^0$ and $(\alpha_2)^0$ are the cross sections for transitions to the first excited levels [26]. Because the asymmetric stretch vibrational level does not change during the transition, its wavefunction remains unchanged as well. The Raman cross section therefore does not depend on the asymmetric stretch quantum number $v_3$.

The cross section of a transition between unperturbed states is calculated by summing the weighted cross-sections of all allowed transitions between the constituent nonperturbed states. As an example, let us consider the transition from $(2 \ell^1 1)_2$ to $(3 \ell^1 1)_1$, with eigenvectors $a$ and $b$ corresponding to the initial and final levels, respectively. The perturbed levels can be written as the following linear combinations:

$$(2 \ell^1 1)_2 = a_{12}(2 \ell^1 1) + a_{23}(3 \ell^1 1) + a_{32}(0 \ell^1 1)
(3 \ell^1 1)_1 = b_{13}(3 \ell^1 1) + b_{12}(2 \ell^1 1) + b_{11}(1 \ell^1 1) + b_{14}(0 \ell^1 1).$$

The unperturbed transitions $(2 \ell^1 1) \rightarrow (3 \ell^1 1), (1 \ell^1 1) \rightarrow (2 \ell^1 1)$, and $(0 \ell^1 1) \rightarrow (1 \ell^1 1)$ are allowed transitions with $\Delta v_1 = 1$, while the transitions $(2 \ell^1 1) \rightarrow (2 \ell^1 1), (1 \ell^1 1) \rightarrow (2 \ell^1 1), (0 \ell^1 1) \rightarrow (0 \ell^1 1)$ are allowed transitions with $\Delta v_2 = 2$. The cross section for the transition between perturbed states $(2 \ell^1 1)_2 \rightarrow (3 \ell^1 1)_1$ is therefore:

$$\langle \alpha \rangle = (\alpha_1)^0 \left( a_{23}^2 b_{11}^2 + a_{22}^2 b_{12}^2 + a_{23}^2 b_{13}^2 \sqrt{1} \right) + \frac{(\alpha_2)^0}{2} \left( a_{22}^2 b_{12}^2 \sqrt{8} + a_{22}^2 b_{13}^2 \sqrt{24} + a_{23}^2 b_{14}^2 \sqrt{48} \right).$$

More generally, the cross section for the transition $(m - 1, \ell, v_3) \rightarrow (m, \ell', v_3)$ is given by:

$$\langle \alpha \rangle = \sum_{i=1}^{m} a_{ii} \left[ (\alpha_1)^0 b_{ii} \sqrt{m - i + 1} + (\alpha_2)^0 b_{i,i+1} \sqrt{i(i + \ell)} \right].$$

where the label $s$ is used for the Fermi-index of the final level to prevent confusion with the Fermi-index of the initial level. A transition between any level $r = 1, 2, \ldots, m$ and $s = 1, 2, \ldots, m + 1$ is allowed as long as $\Delta m = 1$ and the change in the remaining quantum numbers is 0.

Because the $Q$-branch is by far the strongest branch, it is the only one included in this work. The line position of the vibrational transition $(m - 1, \ell, v_3) \rightarrow (m, \ell', v_3)$ is calculated by the difference of the energy of the final and initial state:

$$\nu_0 = E(m + 1, s, \ell, v_3) - E(m, r, \ell, v_3).$$

(A.8)

The line intensity of a single line is given by:

$$I = n_0 P_s P_r \langle \alpha \rangle^2 (\nu_{\text{las}} - \nu_0)^4$$

where $n_0$ is the number density of CO$_2$, $\langle \alpha \rangle$ the Raman cross section, $\nu_{\text{las}}$ the laser wavenumber, $\nu_0$ the line position, and $P_s$ and $P_r$ are the probability that a molecule is respectively in the initial vibrational and rotational state of the transition. The vibrational probability is given by:

$$P_v \equiv \frac{g_v \exp \left( - \frac{E_v}{kT_m} \right)}{Q(T_{v12}, T_{v3})}$$

(A.10)

where $g_v = 1$ if $\ell = 0$, and $g_v = 2$ otherwise. Although our resolution is too low to completely resolve the rotational lines of the $Q$-branch, at high temperatures the spread of rotational lines may be noticeable and is therefore included in the spectral model. Because the $Q$-branch is not fully resolved, instead of calculating the intensity of individual ro-vibrational lines up to an arbitrary rotational level, we introduce here a lineshape that accounts for the rotational spread, given by:

$$g_\mu (\nu) = \left\{ \begin{array}{ll}
\frac{1}{\mu} \exp \left( - \frac{\nu}{\mu} \right), & \text{if } \frac{\nu}{\mu} \geq 0 \\
0, & \text{otherwise}
\end{array} \right.$$

(A.11)

where $\nu$ is the spectral coordinate, $\nu_0$ is the line position, $\mu$ is the rotational spread, which for a Stokes band is given by:

$$\mu = \frac{B' - B''}{kT_{\text{rot}}} \frac{kT_{\text{rot}}}{hc}$$

(A.12)

where $B'$ and $B''$ are the rotational constants of the upper and lower vibrational level respectively, and $T_{\text{rot}}$ is the rotational
temperature. We note that $\alpha$ may be either positive or negative. For an anti-Stokes band, $B^\prime$ and $B^\prime'$ would be interchanged. By using a distribution function for the rotational lines, the expression for the intensity for a single vibrational transition (A.9) changes to:

$$I = m_0 P_\nu (\alpha)^2 (v_{\text{line}} - v_0)^4 g_n (\nu - v_0).$$  \hspace{1cm} (A.13)$$

To find the rotational spread, the rotational constants of the upper and lower levels must be calculated. The rotational constant for a perturbed level with index $r$ are given by the weighted sum of unperturbed rotational constants:

$$B_r = \sum_i m_i^2 B_i^r$$  \hspace{1cm} (A.14)$$

where $m_i^2$ are the coefficients of the eigenvalues, and $B_i^r$ is the rotational constant for the unperturbed level given by:

$$B_i^r (v_1, v_2, v_3) = B_{000} - \sum_i \omega_i v_i + \sum_j \gamma_{ij} v_i v_j$$  \hspace{1cm} (A.15)$$

where $B_{000}$, $\omega_i$, $\gamma_{ij}$ are the Dunham parameters for the rotational constant.

**ORCID iDs**

D C M van den Bekerom [https://orcid.org/0000-0002-7554-2539](https://orcid.org/0000-0002-7554-2539)

A van de Steeg [https://orcid.org/0000-0002-2976-7905](https://orcid.org/0000-0002-2976-7905)

G J van Rooij [https://orcid.org/0000-0003-4795-3274](https://orcid.org/0000-0003-4795-3274)

**References**


[9] van den Bekerom D C M et al 2019 The importance of thermal dissociation in CO$_2$ microwave discharges investigated by power pulsing and rotational Raman scattering *Plasma Sources Sci. Technol.* **28** 055015

[10] Capitelli M et al 2006 Vibrational kinetics, electron dynamics and elementary processes in H$_2$ and D$_2$ plasmas for negative ion production: modelling aspects *Nucl. Fusion** 46


[26] Zilles B and Carter R 1977 *Computer program to simulate raman scattering* NASA-NC-145151 National Aeronautics and Space Administration


[28] Chedin A 1979 The carbon dioxide molecule *J. Mol. Spectrosc.* **76** 430–91