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Nicolas Minesi, Lok Lai, Miles Richmond, Christopher Jelloian, Raymond Spearrin. Shock Tube Study of CO Dissociation for Entry Applications via MHz Rate Laser Absorption Spectroscopy. AIAA AVIATION 2023 Forum, Jun 2023, San Diego, United States. 10.2514/6.2023-3731 . hal-04135544

HAL Id: hal-04135544

<https://hal.science/hal-04135544v1>

Submitted on 21 Jun 2023

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Shock Tube Study of CO Dissociation for Entry Applications via MHz Rate Laser Absorption Spectroscopy

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A shock tube study of carbon monoxide (CO) dissociation was performed at conditions relevant to high-speed entry of Venus and Mars atmospheres. The CO number density (mole fraction) and the temperature is probed behind reflected shock waves at 1 MHz using scanned laser absorption spectroscopy near 2011 cm^{-1} ($4.97\text{ }\mu\text{m}$). The wide range of vibrational states ($v'' = 1, 4, 8,$ and 10) probed by this technique and processed through a Boltzmann population fit allows to perform precise temperature and number density measurements up to and above 9000 K. Mixtures of CO diluted in Ar at 3% – 60% are shock-heated in a wide range of conditions (4,500 – 10,000 K at 0.26 – 4.07 atm) and compared to state-of-the-art chemical kinetic models. Using our measurements (temperature and number density), the rate coefficients of $\text{CO} + \text{M} \rightarrow \text{C} + \text{O} + \text{M}$ for $\text{M} = \text{Ar}$, CO are found to be $k_{\text{diss, CO}} = 1.9 \times 10^{28} \cdot T^{-2.7} \exp(-129,000/T)$ and $k_{\text{diss, Ar}} = 1.5 \times 10^{25} \cdot T^{-2.1} \exp(-129,000/T)$, which compares well with independent experiments across the literature.

I. Introduction

CONVECTIVE and radiative heating on an entry vehicle is particularly sensitive to the atmosphere’s thermochemical state. During Mars and Venus entry, a significant fraction of the mixture is composed of carbon monoxide, CO, which is the major radiation source for speeds above 6 km/s [1]. CO can also be formed in any atmosphere due to the sublimation of the thermal protection of the hypersonic vessel [2, 3]. Despite the critical importance of CO formation and depletion in such environments, there is still some debate regarding its kinetics, especially dissociation. CO dissociation has long been studied using optical diagnostics in shock tubes, but the rate coefficients found by different groups span across several orders of magnitude. In 1994, Park et al. [4] proposed a kinetic mechanism and an elegant solution to simulate vibrational and electronic non-equilibrium. Their model was sufficient to describe the radiation occurring in Mars entry at < 6.6 km/s but was found to be erroneous at higher speeds [5, 6]. This discrepancy renewed the interest in Mars and Venus kinetics during entry and the improvement of CO dissociation rate [6, 7].

At equilibrium, the dissociation of CO becomes significant above 5000 K, which motivates the development of diagnostics near this temperature and higher. Several groups already developed techniques for high-temperature CO sensing: in a steady-state plasma torch, using OES and broadband absorption [2], and in shock tubes, using OES and laser absorption spectroscopy (LAS) [7–13]. At these high temperatures, the characteristic kinetic time is near the μs scale and most of the diagnostics previously demonstrated are not adapted for this time resolution. Single-line scanned LAS with μs -resolution was developed in [7–10] where the temperature (2500 – 10,000 K) was measured relying on Doppler broadening of a CO transition in the infrared (IR). This strategy was however adapted for low-pressure environments where Doppler broadening is the dominating broadening mechanism. A recent study from our group demonstrated measurements at MHz rates of CO mole fraction and temperature via multi-line sensing [14]. The present work leverages this experimental development to perform a kinetic study of CO dissociation across a wide range of temperatures in a shock tube.

This paper is organized as follows. In Section II, the experimental setup and the measurement technique of our previous study [14] are quickly described for context. In Section III, the rate optimization procedure is presented to reconcile simulated and measured species and temperature time histories. Finally, in Section IV, the results of the rate inference are presented and discussed in regard to a review of the available rates in the literature.

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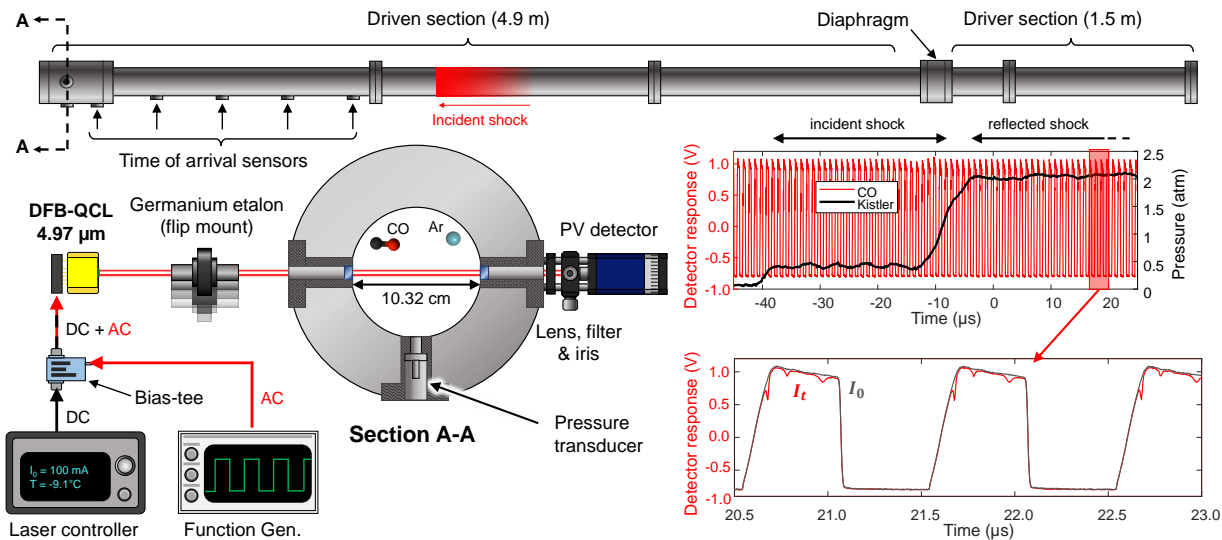


Fig. 1 (Left) Optical alignment setup mounted on the UCLA high-enthalpy shock tube (HEST). (Right) Sample raw detector and pressure measurements. In the inset, the time-resolved measurements (in red) are compared with the averaged background (in grey) [14].

II. Experimental setup and spectroscopy methods

The experimental setup and the methods for fitting the CO absorption lines are described in our previous work devoted to the sensing effort [14] and are summarized here. The UCLA high-enthalpy shock tube (HEST), fully described in [15, 16], is presented in Fig. 1. A 1.5-m driver section is filled with helium until a plastic or metal diaphragm bursts and generates a shock wave in the 4.9-m driven section. Mixtures of CO diluted in argon are manometrically prepared in a stirred mixing tank. The concentration of CO ranges from 3% to 60%. The tank is vacuumed down to less than 20 mTorr before preparing the mixtures. The purity of CO and Ar gases is certified above or equal to 99.99% by Airgas. The combined pressure and pure gas uncertainties result in a relative mixture composition uncertainty always below 0.05%. Thus, the uncertainty of the reference mixture is assumed to be negligible.

The optical setup is schematically presented in Fig. 1. The mean current and temperature of a quantum cascade laser (Alpes Lasers) are regulated using a laser controller (Arroyo 6310). A fixed (DC) current is sent to the laser via the controller, while a 1-MHz modulation is added to this DC component with a bias-tee circuit [17]. In this work, the laser is modulated with a trapezoidal waveform extensively described in [18]. The current amplitude is set to 80% of the maximum allowed by the laser manufacturer. This setting represents a compromise between hardware safety and spectral scan-depth, reaching 1 cm^{-1} . The trapezoidal waveform, shown in Fig. 7, presents a ramp on the increasing side. This ramp prevents the temporal frequency content of the raw electrical signal from being higher than the limiting bandwidth of the detection system (200 MHz) when narrow absorption features are present in the scan. Following the recommendations of [18], we ensured that the equivalent time to scan an FWHM of the CO line is greater than 10 ns (twice the inverse of 200 MHz) to prevent instrument broadening and spectral distortion.

A Voigt lineshape fitting routine is employed to recover absorption areas of the targeted transitions. Four CO transitions – R(8,24), R(10,115), P(4,7), and P(1,25) – are scanned at 1 MHz across $2010.6\text{--}2011.6 \text{ cm}^{-1}$. The CO linestrengths and CO partition function are calculated using the HITEMP 2019 database [19, 20]. Using the areas of these lines, a Boltzmann population fit is performed and provides CO number density and temperature. The fitting procedure is performed assuming equilibrium of the rotational and vibrational temperatures, which is expected in the conditions explored here. Uncertainties in the data processing are calculated according to the methods in [14, 17]. The 1-MHz sampling being extremely fast compared to the timescale of temperature and CO mole fraction evolution, the raw data are processed with a 1- μs resolution but are time-averaged in select conditions. This procedure improved the experimental spectrum signal-to-noise ratio, which in turn reduced the uncertainty (scaling with the square root of the number of measurements). Thus, the uncertainty is typically within 3–5% for number density and 1–3% for temperature.

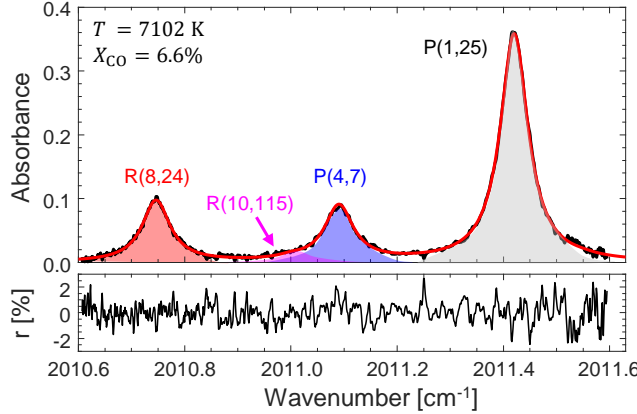


Fig. 2 Typical fit of the CO absorption spectrum between 2010.6 and 2011.6 cm^{-1} [14].

III. Rate optimization

The kinetic mechanism of Johnston and Brandis [7] will be employed to start the optimization and to run the sensitivity analysis. For the present case in a CO and Ar bath, the Johnston and Brandis mechanism is equivalent to the mechanism of Park et al. [4] with an adjustment of the C_2 and CO_2 dissociation rate coefficient. Note finally that this mechanism was recommended at high temperatures by Cruden et al. [7]. It is denoted here as the "baseline mechanism". The baseline mechanism with the modified rate coefficients of (R1) and (R2) is denoted the "modified mechanism". A CANTERA 0-D constant-pressure reactor simulates the shock-heated gas. The reactor pressure and temperature are updated in the simulation time loop according to an isentropic compression law to account for the slight pressure increase measured by the piezoelectric sensor (typically a few mbar/100 μs). In this work, all temperatures (translational, rotational, and vibrational) are assumed to be equal. In the experimental conditions employed in this work, the vibrational-translational (VT) relaxation is always below 0.5 μs [4, 21]. The presence of electronically excited states is neglected (see [22], for instance, for a more refined model). The key reaction rates are identified by sensitivity analysis and an optimization procedure is employed to infer the values of these rates over a range of test conditions.

A. Sensitivity analysis

A sensitivity analysis of reactions with respect to CO mole fraction is conducted and shows that two reactions are largely dominating CO dissociation:



In Fig. 3, the relative impact of the two reactions is shown for a simulated shock at $P_5 = 1$ atm and $T_5 = 9000$ K. Note that these initial temperatures evolve with time as the endothermic dissociation of CO progresses. As could be predicted for a highly diluted CO mixture, CO dissociation is driven by CO-Ar collisions (R2). However, in a mixture of CO:Ar = 60:40, the rate coefficient of CO-CO collisions (R1) is one order of magnitude higher than that of (R2). Therefore, with the experiments performed in this study ranging from 3 to 60% CO dilution, both rate coefficients of (R1) and (R2) are important and can be tuned.

As discussed later in Section IV.B, some work has suggested that the impact of atomic oxygen exchange could be important [23–25]. In that case, CO dissociation would be driven by the following two-step mechanism:



As demonstrated Fig. 3, the sensitivity of CO mole fraction to (R3) is typically one order of magnitude below that of (R1) or (R2). Note that the sensitivity of CO mole fraction to R3 and R4 is the same. This conclusion is in line with the work of Cruden et al. [7] who demonstrated based on fundamental principles that CO dissociation is not driven by O atom exchange, even in undiluted (pure) CO. Thus, for the rest of this work, the rate coefficient of R3 and R4 will remain unchanged.

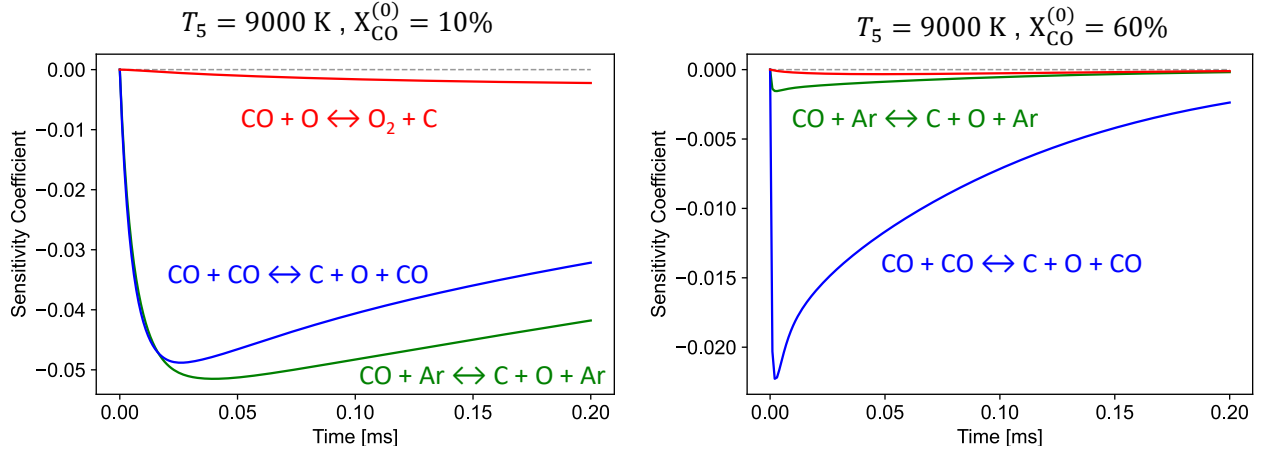


Fig. 3 Sensitivity analysis of CO mole fraction using the baseline mechanism. The simulations are run in a mixture shock-heated at 9000 K and 1 atm where the temperature is allowed to vary due to the endothermic dissociation reactions. The sensitivities are calculated for two mixtures: (left) CO:Ar = 10:90 and (right) CO:Ar = 60:40.

B. Optimization

A range of tests from $T_5 = 4,500$ to 10,000 K was performed in the shock tube and compared to the baseline mechanism. During test times of the order of 100 μs , CO dissociation was noticed above 5000 K via the temperature data. In Fig. 4 from top to bottom, the measured CO mole fraction, X_{CO} , CO number density, $N_{\text{CO}}[\text{cm}^{-3}]$, and temperature, $T[\text{K}]$ are compared to simulated values. Experimentally, N_{CO} and T are calculated from the measured spectra [14]. The mole fraction is calculated from Eq. 1, where $P[\text{Pa}]$ is the pressure and $k_B = 1.38 \times 10^{-23}$ [J/K] is the Boltzmann constant.

$$X_{\text{CO}} = \frac{N_{\text{CO}}}{P/k_B T} \quad (1)$$

In this work, the pressure is calculated in Eq. 2 from the pressure predicted by normal shock relations, P_5 , and accounting for a slight linear increase of pressure measured by the pressure transducer on the shock tube wall, $dp/dt = cst$, multiplied by the time after the reflected shock, t :

$$P = P_5 + (dp/dt) \times t \quad (2)$$

For low-temperature cases and at nearly constant pressure, the drop in temperature induces an overall number density increase which can virtually compensate for the chemical CO depletion. This effect is responsible for the effective increase of N_{CO} in Fig. 4 (left) and is taken into account in the rate optimization.

As shown in Fig. 4, the baseline mechanism under-predicts the reactivity of the mixture: the simulated X_{CO} is always higher than the experimental one. As a consequence, the temperature simulated via the baseline mechanism is also higher than the experimental one. A fitting loop is implemented to reduce the residual, R , between the simulation and the experimental results in both the number density and temperature dimensions, see Eq. 3 where R is the residual, N_{Run} , the total number of experiments, M , the total number of time-resolved data point per shock, $N_{\text{sim}}/T_{\text{sim}}$, the simulated temperature / number density, and $N_{\text{exp}}/T_{\text{exp}}$, the experimental temperature / number density.

$$R = \frac{1}{N_{\text{Run}}} \sum_{\text{Run}} \left[\frac{1}{M} \sqrt{\sum_i^M \left(\frac{N_{\text{CO, sim}}(i) - N_{\text{CO, exp}}(i)}{\Delta N_{\text{CO, exp}}(i)} \right)^2} + \frac{1}{M} \sqrt{\sum_i^M \left(\frac{T_{\text{sim}}(i) - T_{\text{exp}}(i)}{\Delta T_{\text{exp}}(i)} \right)^2} \right] \quad (3)$$

The norm L2 shown in Eq. 3 is normalized by the experimental time-resolved uncertainty, $\Delta N_{\text{CO, exp}}$ and $\Delta T_{\text{CO, exp}}$. This formulation has the advantage to (i) weight equally the optimization by number density and temperature, and (ii) apply more weight to the low-uncertainty measurements. The optimization is run on 39 shocks with conditions spanning across $P_5 = 0.26 - 4.1$ atm, $T_5 = 4500 - 10,000$ K, and $X_{\text{CO}} = 3 - 60\%$. During the loop, the pre-exponential factor and the temperature coefficient of (R2) and (R1) are optimized, whereas the activation energy is kept equal to 129,000 K

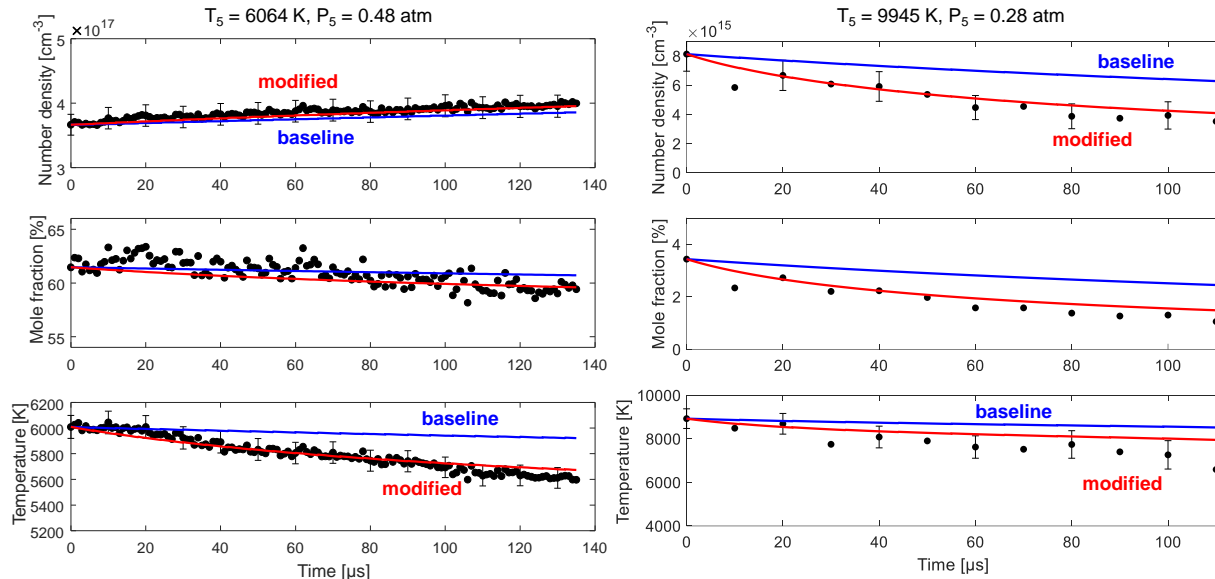


Fig. 4 Typical comparison of the CO dissociation with the baseline mechanism and the modified mechanism. (Left) Low-temperature case for CO:Ar = 60:40. (Right) High-temperature case for CO:Ar = 97:3. The spectra acquired at 1 MHz are time-averaged on a 100-kHz time base (see text).

(= 11.1 eV) [4, 6]. Note that we kept this historical value, although more recent calculations showed that the actual dissociation temperature is 130,462 K [26]. The simulation using the modified rates (i.e. the modified mechanism) is shown in Fig. 4 and follows the trends of temperature and number density evolution more closely than the baseline mechanism. As a consequence, the simulated and experimental mole fractions are also closer across the entire dataset.

IV. Results and Discussion

In this section, the findings of the experimental campaign and the rate coefficient optimization are discussed and compared to the available rates in the literature. First, in Sec. IV.A, the rate coefficients measured experimentally in the literature are reviewed. Then, in Sec. IV.B, recent calculations of the CO dissociation and O exchanges rate coefficients are presented. Finally, in Sec. IV.C, our modified rate coefficients are compared to the aforementioned ones.

A. Previous experimental work on CO dissociation

Carbon monoxide dissociation has been the subject of numerous works summarized here in the following paragraph and Table 1. For context, we repeat here the main reactions of interest, (R1) & (R2), relevant to our experiments performed with CO diluted in Ar.



In 1964, Davies monitored CO dissociation in Ar using the CO fundamental band emission at 4.65 μm , assumed to be proportional to CO concentration [27, 28]. The UV electronic system of CO at 643 nm was also measured and showed similar decay rates. Several studies followed based on optical emission spectroscopy (OES) techniques. Presley, Chackerian, and Watson [29] measured the decay of CO overtone emission ($\Delta v = -2$) to estimate the CO+CO dissociation rate coefficient. Their measurements required to take into account the temperature evolution, which was performed a few years later by Chackerian [33]. The rate coefficient found in [33] was approximately 10 times higher than in [29]. In 1969, Fairbairn [31] was the first to propose that CO* and C₂ could be potential intermediates of CO dissociation. In mixtures of CO and O₂ diluted in Ar, Appleton et al. [32], used the absorption of the 117.6-nm electronic transition of CO to track its number density. They found an apparent CO dissociation energy of 8–8.5 eV, in line with what Davies and Presley found previously and suggesting that intermediates could lower the activation

Author (year)	CO+M	Diagnostic	Wavelength	Incubation	Shock-tube id.	Ref.
Davies (1964)	Ar	OES: CO	643 nm, 4.6 μm	no		[27, 28]
Presley (1966)	CO	OES: CO	2–4 μm	no	30.48 cm	[29]
Fairbairn (1969)	Ar	OES: CO	4.6 μm	yes	3.81 cm	[30, 31]
Appleton (1970)	Ar, O	Absorption: CO	117 nm	yes	7.6 cm	[32]
Chackerian (1971)	CO	OES: CO	2.3–3.6 & 4.6 μm	/	30.48 cm	[33]
Hanson (1974)	CO	Pressure	/	no	7.6 cm	[34]
Mick (1993)	Ar	ARAS: O, C	UV	yes	7.9 cm	[35]
Johnston (2014)	CO, Ar ^(a)	OES: CN, CO	UV	no	10.16 cm	[6]
Cruden (2018)	CO ^(b)	OES: C ₂ , CO	Vis, VUV & IR	no	10.16 cm	[7]
<i>This work</i>	CO, Ar	LAS: CO	5 μm	no	10.32 cm	

^(a) Experiments performed in synthetic Mars atmosphere. During the rate coefficient optimization, the ratio of Ar+CO and CO+CO rate coefficients was kept equal to 15.

^(b) This work did not propose new rates but gave a critical review of the relevance of the available ones based on new experiments.

Table 1 List of experimental CO dissociation experiments performed in shock tubes. Only the dissociative colliders relevant for the present study (M = CO, Ar, C, or O) are shown even if other particles were considered in the references. OES: optical emission spectroscopy, ARAS: atomic resonance absorption spectroscopy, LAS: laser absorption spectroscopy, id.: internal diameter

energy of (R1) and (R2). They also proposed a 4-step dissociation mechanism that could qualitatively explain the results available at that time. Hanson [34] used pressure measurements in pure CO to complement the available dissociation rate coefficients obtained with optical diagnostics. He found an effective CO dissociation rate with a coefficient not compatible with collision theory, see [29], but able to describe his experiments from 5600 to 12,000 K. In 1993, Mick et al. [35] measured O and C number density via atomic resonance absorption spectroscopy (ARAS). Thanks to the high dilution of their experiments ($X_{\text{CO}} < 1\%$) the rate of O and C formation was only sensitive to the Ar+CO dissociation, (R2), and they showed that the fast VT relaxation had rather no impact on the kinetics. Based on the aforementioned works and others, Park et al. [4] proposed a kinetic mechanism to describe shock-heated CO₂-N₂ mixtures, which is still commonly used as a reference.

After a pause of nearly 20 years, a renewed interest in CO dissociation arose because the Park mechanism did not agree with measurements representative of high-speed entry on Venus and Mars [5]. Using the electric arc shock tube (EAST) of NASA Ames [1, 5] with mixtures representative of Mars and Venus, Johnston and Brandis [6] adjusted the rate coefficients of several reactions from the Park mechanism and found better agreement with their new set of data. Motivated by *ab initio* rate coefficients calculated by Schwenke et al. [24] (described later), new experiments were performed on the same shock tube, EAST, by Cruden et al. [7] using pure CO. The measurements of Cruden et al. showed that an electronically excited state of CO is likely an intermediate of dissociation. The radiance measured at multiple wavelengths was found to be in agreement with the model when including the Johnston and Brandis CO dissociation rate above 6.6 km/s (i.e. for high-temperature cases), but was in better agreement with Hanson's one for shock speeds below 6.6 km/s (i.e. for low-temperature cases). To our knowledge, this is the last shock tube study on CO dissociation. All the rate coefficients discussed above are plotted in Fig. 5.

It should be noted that three groups observed so-called "induction time", denoting a delay between the shock wave and the onset of CO dissociation, see Table 1. Fairbairn was the first one to report this effect in [30] and later described the phenomenon thoroughly in [31]. Appleton et al. [32] observed induction times of $\sim 10 \mu\text{s}$ at 8000 K which were in good agreement with the delays reported by Fairbairn. Finally, Mick et al. [35] also observed induction times but an order of magnitude shorter than those of Fairbairn and Appleton. Although this feature was observed with three different optical techniques, it could not be reproduced in the other works reported in Table 1. This effect cannot be explained by a vibrational ladder because VT relaxation is typically 10 to 100 times faster. In our measurements, no induction delay was reported (see also Figure 10 & 11 in our previous work [14]) and for the remainder of this article, the induction period will not be considered.

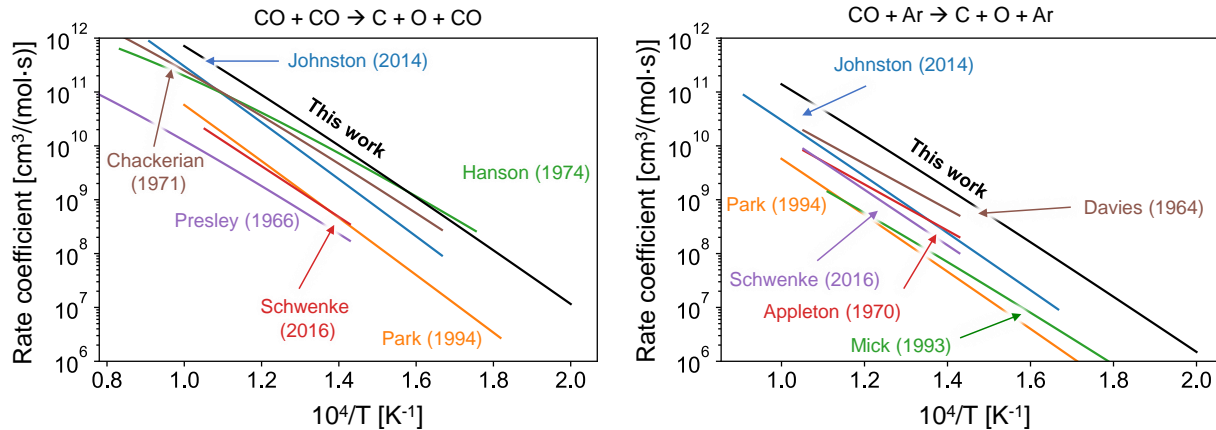


Fig. 5 Comparison of the modified rates (in black) with literature sources for (R1) and (R2).

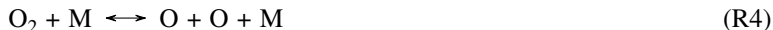
B. Previous numerical work on CO dissociation and CO+O exchange rate

Simulations of CO+M collisions have been performed to describe (i) rotational and vibrational relaxation, (ii) atom exchange, and (iii) CO dissociation - see a summary in Table 2. Fujita [23] calculated *ab initio* the potential energy surfaces of CO + O. From this, he showed that the rotational-translational (RT) and VT relaxation rates are almost equal above 4000 K and proposed a correction to the CO+O VT coefficients of Park [4]. The rate of CO+O dissociation, R5, calculated by Fujita is approximately equal to the rate of CO+Ar dissociation measured by Mick et al. [35].



Thus, Fujita admitted that their calculation could require some refinement because O collisions are typically more reactive than Ar collisions. Nevertheless, they showed that, below 40,000 K, the rate of CO+O exchange, (R3), is faster than CO+O dissociation, (R5). Later, Schwenke et al. [24] calculated new *ab initio* electronic potentials from which they derived CO+Ar dissociation, CO+O dissociation, and CO+O exchange rate coefficients. They also showed that CO+O exchange rate coefficient is higher than that of CO+O dissociation but for temperatures below 16,000 K.

In consequence, in the presence of O atoms, the dissociation of CO could be dominated by the exchange of an O atom, (R3), followed by the dissociation of O₂, (R4).



The impact of these findings could be important for Mars and Venus entry predictions. Indeed, during Mars and Venus entry at 5–8 km/s, the mixture is mostly composed of CO and O due to fast CO₂ dissociation*. Using the electronic potentials calculated by Schwenke et al., Venturi and Panesi [25] showed that in a mixture of CO:O = 50:50, the inclusion of CO+O exchange leads to an acceleration of CO dissociation. As of today, the mechanisms of Johnston and Brandis [6] and Cruden et al. [7] reproduce well the shock-tube data [36, 37] and the measurements performed on MEDLI2 [38, 39]. The rates calculated by Schwenke et al. were found to be coherent with the *experimental data* of Johnston and Brandis, see [40], but were in less good agreement than the *kinetic mechanism* of Johnston and Brandis which was optimized for their data. Therefore the available kinetic mechanisms predict reasonably well the range of conditions explored up to now, but there might need more work to predict correctly the thermochemical state of the plasma during entry at higher speeds.

In this work, the CO+O exchange rate is taken from Park [4] (as done in [6, 7]). As described in the previous paragraph, this rate could be improved. However, the sensitivity analysis showed that (R3) and (R4) do not influence CO number density in our case, see Fig. 3, because our study is performed on CO diluted in Ar. We note however that in pure CO₂, the impact of (R3) and (R4) would be higher, but this study is left for future work.

Author (year)	CO+M	Method	Ref.
Fujita (2008)	O diss., O exc.	QCT	[23]
Schwenke (2016)	O diss., O exc., Ar	QCT	[24]
Venturi (2018)	to-do	CG-QCT	[25]

Table 2 List of numerical studies relevant for the kinetics of CO dissociation. QCT: quasi-classical trajectory, CG-QCT: coarse-grain QCT.

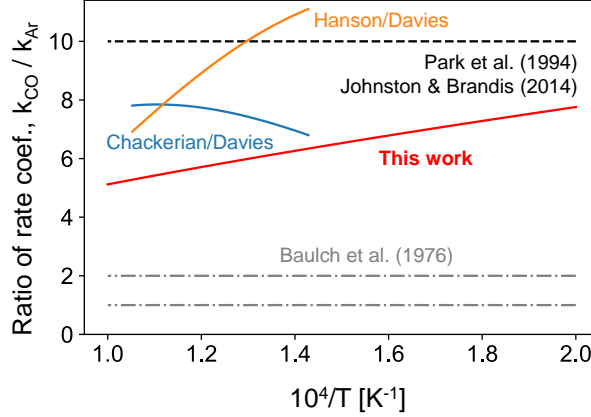


Fig. 6 Comparison of the relative dissociation efficiencies of CO and Ar found in this work (in red) and the one assumed constant in the mechanism of Park et al. [4] and Johnston and Brandis [6] (in dashed black). The relative dissociation efficiency is also shown by taking the rate coefficients of other authors who published before 1994 [27, 33, 34] and the recommendations of Baulch et al. [41].

C. Comparison of the present rate coefficient with the literature

The modified rate coefficients calculated via our optimization procedure are shown in Fig. 5 and given here:

$$k_{\text{diss, CO}} = 1.9 \times 10^{28} \cdot T^{-2.7} \exp\left(\frac{-129,000 \text{ K}}{T}\right) \quad (4)$$

$$k_{\text{diss, Ar}} = 1.5 \times 10^{25} \cdot T^{-2.1} \exp\left(\frac{-129,000 \text{ [K]}}{T}\right) \quad (5)$$

The rate coefficient of CO + CO, (R1), is above the coefficient of Park by a factor of 10. This difference is expected since, in CO₂ atmospheres, the Park mechanism overpredicted the CO emission because of a too-low dissociation rate [6]. Our modified rate coefficient favors the results of Johnston and Brandis [6] at high temperatures and that of Hanson [34] at low temperatures, which is in complete agreement with the findings of Cruden et al. [7]. We also note that our rate coefficient is in close agreement with that of Chackerian [33]. As such, the rate coefficient found in the present work is expected to reasonably match the radiation measurements of [7].

Our proposed rate coefficient of CO+Ar, (R2), is five times higher than that of Johnston and Brandis, which is at the edge of their error bound. Notably, at 7000 K, our rate coefficient for CO+Ar is within a factor of two to the historical one of Davies [27]. As shown in Fig. 6, the ratio $k_{\text{diss, CO}}/k_{\text{diss, Ar}}$ is found to be equal to 6.2 on average. This ratio is close to the value of 10 chosen by Park et al. [4] and later reused by Johnston and Brandis [6]. At that time, Park et al. used a ratio of 10 because this ratio was also employed for CO₂ dissociation by Ar and molecules. Note however that the compendium of Baulch et al. [41] suggests to rather use a ratio of 1 – 2 based on the data of Appleton et al. [32] and Presley et al. [29]. Using the data of Hanson and Davies in Fig. 6 indicates that a ratio of 10 was a legitimate

*Estimations based on those presented by Schwenke et al. [24] for entry speeds of 5–8 km/s.

approximation. However, using the data of Chackerian and Davies provides an average ratio very similar to ours, which indicates that the ratio of the two rate coefficients determined in this work is reasonable.

V. Conclusions

Laser absorption spectroscopy was employed to measure CO number density and temperature in a shock-heated CO in a bath of Ar. These measurements were shown to be a sensitive method for studying high-temperature chemistry and determining the CO rate of dissociation due to collisions with $M = \text{Ar}$ or CO in $\text{CO} + M \rightarrow \text{C} + \text{O} + M$. The influence of O atom exchange is found to be negligible in our conditions. The measured dissociation rate coefficients lie within the uncertainty limits of the coefficients found by Johnston and Brandis [6]. Moreover, the CO+CO dissociation rate coefficient of this study is in very close agreement with Johnston and Brandis near 10,000 K, and with Hanson [34] near 4,000 K, which was the conclusion of the recent emission measurements performed by Cruden et al. [7] in shock-heated undiluted CO. In future work, the analysis of shock tube measurements performed at higher temperatures will be performed to extend the range of validity of the present rate coefficients and will be associated with an estimation of the rate coefficient uncertainties.

Acknowledgment

This work was sponsored by NASA's Space Technology Research Grants Program via an Early Career Faculty award 80NSSC21K0066. The authors thank Anil Nair and Nick Kuenning for their help in the shock tube operation and for insightful discussions about these experiments. The authors also thank Brett Cruden, Megan Macdonald, and Augustin Tibère-Inglesse at NASA Ames for their feedback about this work.

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