

High-Temperature Line Strengths with He- and Ar-Broadening Coefficients of the P(20) line in the $1 \leftarrow 0$ band of Carbon Monoxide

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1 Introduction

Tunable mid-infrared laser absorption spectroscopy is a very powerful tool for highly selective and sensitive measurements used for the detection and monitoring of various specific molecular species in chemically reacting gas mixtures. This robust technology is a non-intrusive method capable of monitoring gas species in real time due to absorption features through the electromagnetic spectrum exhibited by the molecules since a specific light wavelength can be employed to quantify a targeted species. One of these species is carbon monoxide, CO. *In-situ* measurements of CO concentration in reacting gases in shock-tube kinetics studies have been conducted with several absorption features of carbon monoxide. In our experiments, the combination of a tunable quantum cascade laser with a shock tube permits the monitoring of a species' concentration for 3 ms at high temperatures. In particular interest to this paper is the P(20) line in the $1 \leftarrow 0$ band of carbon monoxide (CO), which has been employed for multiple studies [1-5]. Rudolph *et al.* utilized the P(20) line located at the wavelength of 2059.91 cm^{-1} to quantify the CO mole fraction during dry methane reforming to evaluate existing models under polygeneration-type conditions [2]. Similarly, Mathieu *et al.* carried out experiments to understand the combustion properties of ethanol pyrolysis and its dry reforming with CO₂ [3]. Additionally, common constituents of the liquid electrolyte in lithium-ion batteries were studied in pyrolysis conditions [5] with the fire suppressant characteristics of the bis(2,2,2trifluoroethyl) carbonate also investigated [4] for electric vehicle applications. To probe and assess the validity of modern detailed kinetics mechanisms, these studies performed experimental measurements using highly diluted mixtures, as it allows for a minimal increase in the temperature, essentially producing results only driven by the chemical kinetics. The diluent compounds are typically helium (He) and argon (Ar). He is added to the Ar to expedite the vibrational relaxation of CO [6]: experimentally, CO is formed in the ground state but is then excited to its vibrational equilibrium, which takes up to a few hundred microseconds. On the other hand, models are state-independent, meaning that they assume the species are at their vibrational equilibrium. Thus, to really compare the data to the models, one needs to have the molecules at their equilibrium state. He is added to the mixture as it is an efficient collider, and so the vibrational relaxation time is brought down to a few microseconds. Hence, accurate CO absorption coefficients that account for He-related broadening are necessary when using mixtures containing helium.

The present work is organized as follows: the experimental method introduces the shock-tube facility, and the scanning laser absorption materials. The Results section presents the linewidths that were determined at room and high temperatures, whilst direct measurements of $\gamma_{CO-He}(T_0)$ and $\gamma_{CO-Ar}(T_0)$ as well as the temperature-dependent coefficients n_{CO-He} and n_{CO-Ar} were also determined.

2 Experimental Method

2.1 Shock-Tube Facility

A high-purity, stainless-steel shock tube was used to study shock-heated, CO broadening parameters. A shock tube generates a shock wave using a driver section of high-pressure gas and a driven section of low-pressure gas separated by a diaphragm. The driven section has a length of 7.88 m and an internal diameter of 16.2 cm, while the driver section has a length of 3.25 m and an internal diameter of 7.62 cm. They are separated by a polycarbonate diaphragm and a cross-shaped cutting blade to facilitate the diaphragm's rupture. When the diaphragm opens, the high-pressure driver gas (Helium in the present case, due to its high efficiency) quickly expands into the driven gas and forms a contact surface that acts like a piston. This compression initiates a shock wave propagation, that reflects from the endwall of the shock tube and causes heating of the test gas. The velocity of the incident shock wave is measured with five fast-response, piezoelectric pressure transducers over the last 130 cm of the driven section, permitting the detection of the shock passage. With a well-known spacing between them, the velocity of the shock wave is measured and extrapolated to the endwall. Using the initial temperature and pressure conditions as well as the incident shock wave velocity at the endwall location and the initial composition of the mixtures, the post reflected-shock conditions, T_5 and P_5 , respectively, were calculated using the 1-D normal shock equations. The tube was pumped down to at least 10^{-3} Pa with a system consisting of a vane pump and a turbomolecular pump before each experiment to ensure high purity of the measurements.

Two mixtures were considered in this study to obtain broadening parameters from He and Ar, the major dilution components in [2-4]: 0.006 CO/He and 0.006 CO/0.01H₂/Ar, as recommended in a similar broadening parameter study [7] that ensure a proper vibrational relaxation time of CO. In the first case, helium reduces the vibrational relaxation time as discussed previously. In the second case, the small addition of 1% H₂ in the mixture significantly decreases the vibrational relaxation time, compensating for the absence of He. Mulvihill *et al.* [7] compared the 0.006 CO/0.01H₂/Ar mixture without H₂ and computed vibrational times according to Millikan and White [8]. One can see that without H₂ the vibrational time is 13.5 times longer at 1300 K and 3.8 times longer at 2100 K, for instance. The experimental conditions covered during the course of this study are summarized in Table 2: due to the large difference between the He and Ar impact, two diaphragm thicknesses were needed to achieve similar post-reflected shock pressures and temperatures, namely 2.03 mm and 0.127 mm for He and Ar, respectively.

2.2 Scanning Spectroscopy

A tunable quantum cascade laser with a range of 2056 – 2064 cm⁻¹ was scanned at 1.5 kHz to target the P(20) line at 2059.91 cm⁻¹. Again, two mixtures were prepared to identify the broadening parameters of He and Ar, respectively: 0.006 CO/He and 0.006 CO/0.01H₂/Ar, based on the Mulvihill *et al.* previous work on the R(12) transition line for CO [7]. The laser is controlled using a dual temperature and current controller (Arroyo 6310-QCL). While a stable temperature of 30°C is applied, a function generator (Stanford Research System DS340) provides a saw-tooth voltage signal adjusted at 3.9 V with a 50 mA/V parameter, suitable to detect the P(20) line usually observed with the following features: 30°C and 196 mA, see [2,3] for more details. The wavelength characterization is possible by recording the voltage signal behavior passing through the shock tube containing the mixture to be studied and the interference signal generated when a Fabry-Perot etalon is placed in the path of the laser light. Capturing the etalon fringe peaks permits a third-order polynomial fit that can convert the scan time to the relative

frequency. Thus, a solid germanium etalon of length 5.08 cm with a free spectral range (FSR) of $0.025 \text{ cm}^{-1} \pm 0.001 \text{ cm}^{-1}$ was selected. Therefore, the laser was split into two intensities denoted I_t and I_{etalon} using a ZnSe beam splitter that were collected into two distinct, cryogenically cooled HgCdTe photovoltaic detectors. Figure 1 illustrates the I_t and I_{etalon} signals along with the pressure trace for the mixture 0.006 CO/He and post-shock conditions of 1412 K and 70.3 kPa. The detector bandwidth and sampling rate were able to adequately capture the shape of the spectra with a spectral resolution of 0.001 cm^{-1} and a peak-to-peak voltage of 0.6 V.

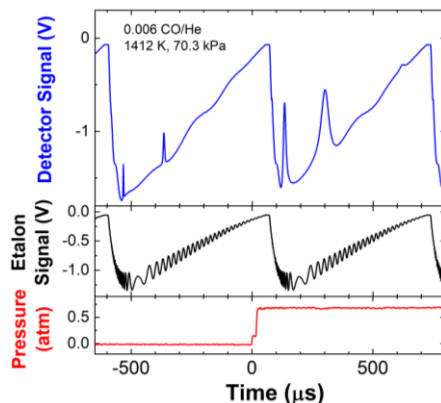


Figure 1: Scanned-wavelength experiment showing: a) the transmitted signal of a 0.006 CO/He mixture at 1412 K, 70.3 kPa, b) the etalon signal used as a ruler (germanium, $\text{FSR} = 0.025 \text{ cm}^{-1} \pm 0.001$), and c) the sidewall pressure.

3 Preliminary Results

Two mixtures, each containing 6,000 ppm of CO diluted in He and 1% H_2/Ar , respectively, were scanned near 2059.91 cm^{-1} at 296 K over a pressure range from 0.7 kPa to 8.0 kPa. Figure 5 presents the absorbance measurements where the peaks of the absorbance profiles are centered to the P(20) transition line of CO. As one can see, the absorbance increases when more pressure from both mixtures is introduced within the shock tube: the CO species is therefore able to absorb the laser light during 16.2 cm (the inner diameter of the shock-tube facility), while the perturbing species impact the shape of the profiles significantly. The perturbing species He exhibits a larger broadening effect: when the widths at half maximum of the profiles are compared, He gives values 6% higher than Ar.

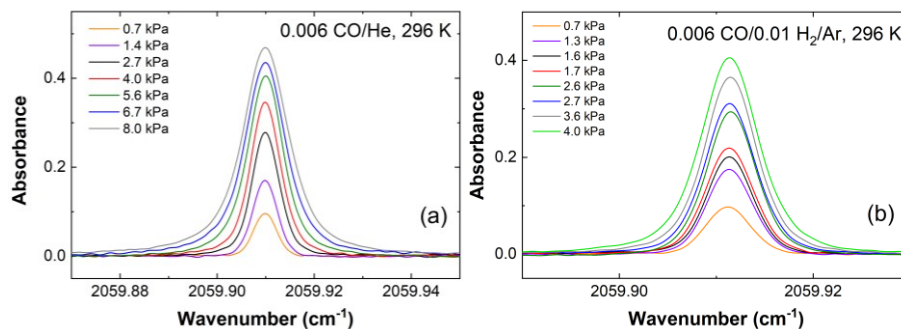


Figure 2: Absorbance measurements for the transition near 2059.91 cm^{-1} of the P(20) line in the $1 \leftarrow 0$ band at 296 K for a) 0.006 CO/He, pressure range from 0.7 kPa to 8.0 kPa, and b) 0.06 CO/0.01 H_2/Ar , pressure range from 0.7 kPa to 4.0 kPa.

From these measurements carried out at room temperature, the objective was to obtain the line strength $S_{12}(T_0)$ as well as the absorption coefficients $\gamma_{\text{CO-He}}(T_0)$ and $\gamma_{\text{CO-Ar}}(T_0)$ for He and Ar, respectively. Along the way, verification using literature results validated the current method used

herein. Figure 3 illustrates the integrated areas for our experiments: as the CO concentrations are the same for both mixtures, the integrated absorbances correlate in one linear fit (dashed line). A mixture of 5,000 ppm CO in 0.01 H₂/Ar from Ren *et al.* [9] scanning for the P(20) line also depicts a linear increase of the integrated absorbance when the pressure is increased, and is located below our results in Fig. 3.

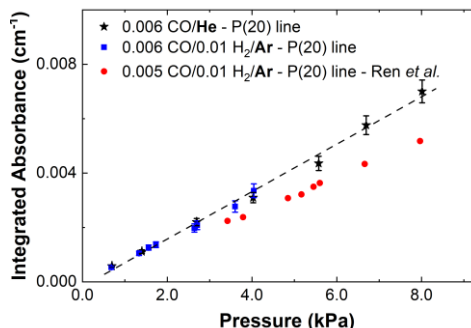


Figure 3: Pressure dependence of integrated absorbance compared to 0.005 CO/0.01 H₂/Ar from [9].

The line strengths are directly extrapolated from the profiles presented in Fig. 2, and the averaged measurement of $S_{12}(T_0)$ is $0.854 \text{ cm}^{-2}\text{-atm}^{-1}$ ($\pm 4\%$), which agrees with the HITEMP prediction of $0.865 \text{ cm}^{-2}\text{-atm}^{-1}$ ($\pm 2\%$) and the measurement from the Ren *et al.* [9] work of $0.872 \text{ cm}^{-2}\text{-atm}^{-1}$ ($\pm 2.5\%$). The broadening coefficients due to collisions from the perturbing species He and Ar on CO absorption are extrapolated for our new results. Pseudo-Voigt fits were applied to the measured spectra, as can be seen in Fig. 4, for sample absorbance measurements at 296 K, and 2.7 kPa for the mixtures 0.006 CO/He and 0.006 CO/0.01 H₂/Ar. The best Voigt-fits are presented with the residuals and good agreement is observed between the experimental spectra and the normalized Voigt fit, leading to a value for $\gamma_{CO-Ar}(T_0)$ of $0.040 \text{ cm}^{-1}\text{-atm}^{-1}$, corroborating the literature results ranging from 0.0395 [9,10] to 0.0415 $\text{cm}^{-1}\text{-atm}^{-1}$ [11], and a value for $\gamma_{CO-He}(T_0)$ of $0.053 \text{ cm}^{-1}\text{-atm}^{-1}$.

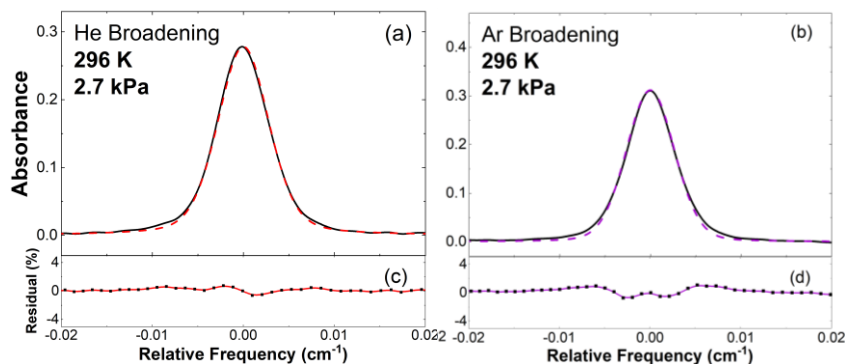


Figure 4: Representative experimental line shapes, best-fit Voigt profiles, and residuals at 296 K, 2.7 kPa for the mixture of (a-c) 0.006 CO/He and (b-d) 0.006 CO/0.01 H₂/Ar.

Absorbance measurements at higher temperatures, namely 1192 K, 111.5 kPa and 1445 K, 74.5 kPa, are shown in Figs. 5 (a-d) for the mixtures 0.006 CO/He and 0.006 CO/0.01 H₂/Ar, respectively. Good agreement is observed between the experimental spectra and the normalized Voigt fit, leading to the extrapolation of the temperature-dependent coefficients n_{CO-He} and n_{CO-Ar} of 0.983 and 0.618 for He and Ar, respectively. While n_{CO-Ar} is in good agreement with the Ar coefficient of 0.639 from the Ren *et al.* study [9], the theoretical value of 0.463 for He from the Predoi-Cross *et al.* work [12] differs by 53% with the new coefficient $n_{CO-He} = 0.983$ obtained herein. It is noteworthy to mention that the Predoi-Cross line parameters were retrieved for temperatures between 79 and 296 K, and are subjected to out-of-domain temperature discrepancies when evaluated against shock tube temperature conditions.

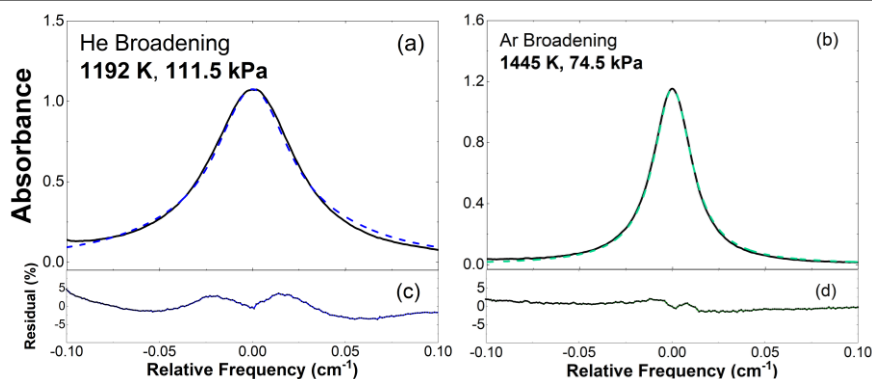


Figure 5: Representative experimental line shapes, best-fit Voigt profiles, and residuals in a mixture of (a-c) 0.006 CO/He at 1192 K, 111.5 kPa, and (b-d) 0.006 CO/0.01 H₂/Ar at 1445 K, 74.5 kPa.

An uncertainty analysis is performed and the results are summarized in Fig. 6. It consists of perturbing several factors that are part of CO scanning results and noting the change that echoes in the measurements. Three parameters are obtained in this study: the linestrength at T_0 ($S_{12}(T_0)$), the broadening coefficient at T_0 ($\gamma(T_0)$), and the temperature exponent (n) for both He and Ar. The $S_{12}(T_0)$ is impacted by five major contributors: the initial temperature T ($296 \text{ K} \pm 2 \text{ K}$), the path length L ($16.2 \text{ cm} \pm 0.1 \text{ cm}$), the initial pressure P ($0.7\text{-}8 \text{ kPa} \pm 0.01 \text{ kPa}$), the integrated area A (2% uncertainty), and the CO initial concentrations X_{CO} (3% uncertainty). The temperature shows its maximum uncertainty of 2.58% and 4.16% for He and Ar, respectively. Similarly, the collisional broadening factor $\Delta\nu_c$ (2%, based on residuals), along with T , P , and X_{CO} have been tested and give uncertainties between 0.1% (X_{CO} for both He and Ar), and 2.38% (P) for He and 2.57% ($\Delta\nu_c$) for Ar. Lastly, T_5 (0.8% uncertainty), P_5 (1% uncertainty), $\gamma(T_0)$, and $\gamma(T)$ with both 5% uncertainty, based on residuals, have a noticeable effect on the temperature-exponent. The $\gamma(T_0)$ and $\gamma(T)$ demonstrate the maximum uncertainty contribution by 3.58% and 5.25% for He and Ar, respectively.

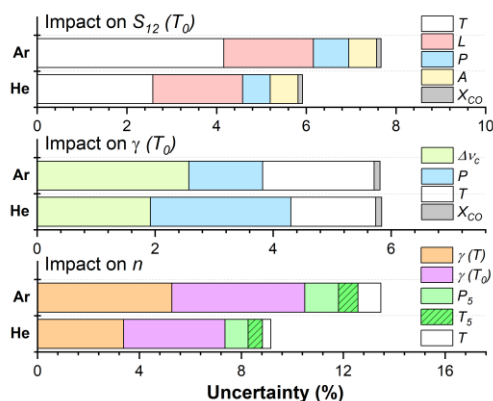


Figure 6: Uncertainty analysis of the P(20) transition line showing the contribution of major parameters.

4 Conclusion

Scanning experiments were performed for the P(20) line in the $1 \leftarrow 0$ transition band of CO at 2059.91 cm^{-1} . While a line strength of $0.854 \text{ cm}^{-2}\text{-atm}^{-1}$ was measured at 296 K using two mixtures (0.006 CO/He and 0.006 CO/0.01 H₂/Ar), high-temperature measurements between 1100 and 2800 K, and for pressures from 24.7 up to 147.4 kPa behind reflected shock waves were carried out. $\gamma_{CO-He}(T_0)$ and $\gamma_{CO-Ar}(T_0)$ at room temperature were determined to be $0.053 \text{ cm}^{-1}\text{-atm}^{-1}$ and $0.040 \text{ cm}^{-1}\text{-atm}^{-1}$, respectively. Moreover, the temperature-dependent coefficients n_{CO-He} and n_{CO-Ar} were extrapolated to be 0.983 and 0.618, respectively.

References

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