Gas-phase Boudouard disproportionation reaction between highly vibrationally excited CO molecules

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Abstract

The gas-phase Boudouard disproportionation reaction between two highly vibrationally excited CO molecules in the ground electronic state has been studied in optically pumped CO. The gas temperature and the CO vibrational level populations in the reaction region, as well as the CO2 concentration in the reaction products have been measured using FTIR emission and absorption spectroscopy. The results demonstrate that CO2 formation in the optically pumped reactor is controlled by the high CO vibrational level populations, rather than by CO partial pressure or by flow temperature. The disproportionation reaction rate constant has been determined from the measured CO2 and CO concentrations using the perfectly stirred reactor (PSR) approximation. The reaction activation energy, 11.6 ± 0.3 eV (close to the CO dissociation energy of 11.09 eV), was evaluated using the statistical transition state theory, by comparing the dependence of the measured CO2 concentration and of the calculated reaction rate constant on helium partial pressure. The disproportionation reaction rate constant measured at the present conditions is \( k = (9 \pm 4) \times 10^{-18} \text{ cm}^3/\text{s} \). The reaction rate constants obtained from the experimental measurements and from the transition state theory are in good agreement.

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1. Introduction

The CO disproportionation reaction (Boudouard reaction),

\[
\text{CO} + \text{CO} \rightarrow \text{CO}_2 + \text{C}
\]

is one of key free carbon formation processes occurring both in high-temperature gas flows and in non-equilibrium electric discharges. This reaction has long been observed at high temperatures on oxidized surfaces such as iron oxide in the process known as metal dusting [1], which leads to corrosion of metal surfaces and has been of great concern in various industrial processes. The mechanism of this reaction is still debated and includes two possible scenarios. In the first scenario, a reaction takes place between two CO molecules absorbed on the surface, while the second scenario involves a reaction between a gas-phase CO molecule and an adsorbed CO molecule. In the surface reaction of Eq. (1), the activation barrier is considerably reduced from the gas phase values, which appear to exceed at least 140 kcal/mole, although significant surface reaction still requires rather high temperatures [1–13]. The theoretical study of this disproportionation on surfaces of transition metal oxides by Cheng et al. [3] indicates that the second scenario is the totally dominant channel. Going beyond near-thermal equilibrium reaction, the enhanced reactivity of highly vibrationally excited molecules on metal surfaces is a well-known effect. There is evidence [4] that vibrational excitation of CO leads to production of CO2 on surfaces (primarily copper oxide) at significantly lower temperatures, below 200 °C. At these temperatures, thermal equilibrium reaction on the same surface shows no detectable CO2 production [4]. This suggests that vibrational excitation may contribute into overcoming the activation energy of the CO disproportionation reaction.
In the gas phase, reaction of Eq. (1) has been observed in a glow discharge \[5,6\] and in experiments on isotopic enrichment of \(^{13}\)C using ultraviolet photolysis of carbon monoxide \[7–9\]. In both cases, it has been concluded that the mechanism responsible for the CO$_2$ production involves metastable CO\(a^3\Pi_r\) molecules produced by either electron impact excitation of CO (in a glow discharge) or by resonance absorption of the 206.22 nm iodine atom line generated by a flash lamp (in UV photolysis),

$$\text{CO}(a^3\Pi_r) + \text{CO} \rightarrow \text{CO}_2 + C.$$  \hfill (2)

The activation energy of reaction of Eq. (2) is believed to be close to the excitation energy of the \(a^3\Pi_r\) electronic state, approximately 6 eV (140 kcal/mole) \[5,9\], and is about half of the CO dissociation energy of 11.09 eV. The rate constant of this reaction was estimated to be \(k_{a^3\Pi}(a^3\Pi) = 1.3 \times 10^{-12} \text{ cm}^3/\text{s}\), based on the concentration of CO\(a^3\Pi_r\) and the rate of CO$_2$ production in a glow discharge \[5\]. The effect of vibrationally excited CO molecules, which were also present in the discharge, on the rate of the disproportionation reaction was not studied. A similar rate constant, \(k_3(a^3\Pi) = 1.9 \times 10^{-12} \text{ cm}^3/\text{s}\), was reported in the UV photolysis experiments \[9\].

The gas-phase disproportionation reaction which does not involve electronically excited species may only occur if the activation barrier is overcome at the expense of the translational or the vibrational energy of the reactants. The former channel would require extremely high gas temperatures available only in shock tube experiments, which is the main reason why Boudouard disproportionation reaction is not commonly observed in the gas phase. On the other hand, temperatures behind strong reflected shocks are sufficiently high to induce chemical reactions in carbon monoxide \[10–13\]. In particular, Mick et al. \[13\] have studied CO decomposition behind the reflected shock by monitoring the time-dependent concentrations of C and O atoms, assuming that CO dissociation

$$\text{CO} + \text{M} \rightarrow \text{C} + \text{O} + \text{M},$$  \hfill (3)

(M = Ar or CO) is the dominant chemical reaction. We note that the Arrhenius fit to the reaction rate constant measured in Ref. \[13\], assuming the activation energy equal to the CO dissociation energy, 11.09 eV, yields a strong inverse temperature dependence of the pre-exponential factor, \(T^{-3.1}\). This indicates that an alternative reaction channel, with a considerably lower activation energy, may affect the measured reaction rate. Interestingly enough, the Arrhenius fit with the activation energy near 6.0 eV gives more reasonable pre-exponential factor temperature dependence, near the collision-frequency dependence of \(T^{0.5}\) \[4\]. This result suggests that the disproportionation reaction of Eq. (2), rather than CO dissociation reaction of Eq. (3), may in fact be the dominant reaction channel during high-temperature CO decomposition behind shock waves.

It has been previously suggested \[14\] that in the gas phase, the Boudouard disproportionation reaction may also occur at low temperatures, in collisions of highly vibrationally excited CO molecules in the ground electronic state,

$$\text{CO} + \text{CO} \rightarrow \text{CO}_2 + C,$$  \hfill (4)

prepared by optical pumping of carbon monoxide by resonance absorption of CO laser radiation,

$$\text{CO} + h\nu \rightarrow \text{CO}(v+1).$$  \hfill (5)

However, the rate coefficient of reaction of Eq. (4) was estimated to be low, <10$^{-10}$ cm$^3$/s. During optical pumping, only the low states of CO, \(v < 10\), are populated by resonance absorption, while higher vibrational levels of CO, \(v > 10\), which are not directly coupled to the laser radiation, are populated by the anharmonic vibration–vibration (V–V) exchange processes \[15,16\],

$$\text{CO}(v) + \text{CO}(w) \rightarrow \text{CO}(v+1) + \text{CO}(w+1), \quad w > v.$$  \hfill (6)

In previous CO optical pumping experiments \[17–20\], vibrational levels up to \(v \approx 40\) were detected, which corresponds to a vibrational energy of up to 7.7 eV. Note that in electric discharges, where both electronically excited and highly vibrationally excited CO molecules are created by electron impact, the reaction channel of Eq. (4) may be obscured by reaction of Eq. (2). On the other hand, in the optically pumped CO, in the absence of an externally applied electric field, direct excitation of electronic levels by electron impact is a minor factor compared to electric discharges. Although UV emission from electronically excited CO has been observed in previous optical pumping experiments, such as 4th positive bands CO\(A^1\Pi \rightarrow X^3\Sigma^+\) \[17,19,21,22\] and 3rd positive bands CO\(b^3\Sigma^+ \rightarrow a^3\Pi_r\) \[21\], the measured population of the electronically excited CO\(A^1\Pi\) state was low, \(10^{10} – 10^{13} \text{ cm}^{-3}\) \[19\]. Population of the metastable CO\(a^3\Pi_r\) state in the optically pumped CO, although never measured in the experiment, is also likely to be low because of a very effective collisional quenching mechanism

$$\text{CO}(a^3\Pi_r) + \text{CO} \rightarrow \text{CO}(w) + \text{CO}(v),$$  \hfill (7)

with a rate coefficient of \(\sim 10^{-10} \text{ cm}^3/\text{s}\) \[23\]. This makes optically pumped CO an ideal environment to study reaction of Eq. (4).

The main objective of the present work is to study kinetics of reaction of Eq. (4) in optically pumped CO, to measure its rate coefficient, and to determine whether CO disproportionation may efficiently occur in a reaction between two vibrationally excited CO molecules in the ground electronic state.

2. Experimental setup

A schematic of the experimental setup is shown in Fig. 1. A carbon monoxide (CO) laser is used to vibrationally excite CO, initially at room temperature, in the flowing reactor (see Fig. 1). The CO laser used in the present experiments is a cw liquid nitrogen cooled, electric discharge
excited gas laser capable of lasing on multiple lines in broadband mode. Typically, the gas mixture composition and discharge conditions in the laser are optimized to produce a substantial fraction of its output on the $v = 1 \rightarrow 0$ and $v = 2 \rightarrow 1$ fundamental band transitions, which is necessary for the laser beam absorption by carbon monoxide in the reactor, initially at room temperature. The present use of CO laser pumped absorption to study energy transfer processes in molecular gases at conditions of extreme vibrational disequilibrium is a further development of a technique with a considerable literature [14–22,24].

The continuous flow reactor is a six-arm glass cell with a total volume of approximately 112 cm$^3$. The reactor contains the gas mixture of CO, Ar, and He flowing at a very slow flow rate, 24 cm$^3$/s. The pressure inside the reactor is kept constant, $P = 110$ Torr. The flow rates of all the gases are measured by rotameters upstream of the reactor. The focused laser beam enters and exits the reactor through 1 in. diameter CaF$_2$ windows, as shown in Fig. 1. The arm used to let the CO laser beam into the reactor is purged by argon flow to prevent the laser beam absorption by CO and resultant carbon deposit on the window. A cylindrical glass tube with a 5 mm diameter hole at one end blocks carbon monoxide in the reactor from entering the purged region (see Fig. 1). The transmitted laser beam power is measured by a power meter placed at the opposite arm of reactor (see Fig. 1).

Spontaneous infrared emission from carbon monoxide vibrationally excited by the CO laser beam absorption is collected at 90° through another CaF$_2$ window, as shown in Fig. 1. The CO fundamental, first overtone, and second overtone emission from the vibrationally excited, chemically reacting region is collected by an off-axis parabolic mirror and focused into an emission port of an IFS-66 Bruker Fourier transform infrared spectrometer. The first overtone CO emission spectra are used to infer the CO vibrational distribution function (VDF) and the translational/rotational temperature of the flow in the reaction zone. The response function of the FTIR detector and collection optics was measured using a calibrated blackbody course (InfraRed Industries Inc, Model 201). First, the R branch of the $1 \rightarrow 0$ band of the CO fundamental spectrum was used to infer the translational–rotational temperature in the reaction zone. Self-absorption may be a significant factor at relatively high CO partial pressures in the cell (3–12 Torr) and long optical path (~10 cm). For this reason, emission from high rotational levels, $J = 30–40$, was used to infer the rotational temperature. Then, the CO first overtone spectrum was used as an input in a computer code [20] to infer the VDF. Basically, the code infers relative populations of CO vibrational levels using the least squares fit of a synthetic infrared spectrum to a high-resolution experimental spectrum, at a known temperature.

The mixture of chemical reaction products flowing from the reactor passes through an absorption cell mounted in a sample compartment of the same FTIR. Infrared absorption spectra of CO$_2$ present in the product mixture are measured by the FTIR using an internal infrared source (globar) and calibrated using CO$_2$-Ar mixtures of known composition at the same pressure, $P = 110$ Torr. The calibrated CO$_2$ absorption spectra are used to measure absolute concentrations of carbon dioxide produced in the reactor. Since the FT spectrometer can only perform one measurement (emission or absorption) at a time, the emis-
sion and absorption measurements were performed in a quick succession one after the other and then repeated. For the absorption measurements, a low spectral resolution of 2 cm$^{-1}$ was used, whereas high-resolution emission spectra (0.25 cm$^{-1}$) were used to infer the flow temperature and the VDF. Each measurement consisted of 24 FTIR scans to improve the signal to noise ratio.

Small amounts of CO$_2$ and water vapor present inside the absorption compartment of the FTIR presented a challenge. A commercial purge system (Puregas, model PCDA), was used to remove water and carbon dioxide from the FTIR. Since it was found that some CO$_2$ was still present in the system, the spectrometer was additionally purged with nitrogen. Although we were unable to completely remove CO$_2$ leaking into the spectrometer from the atmosphere, background absorption (with the absorption cell pumped down below 0.1 Torr) was measured and then subtracted from each CO$_2$ absorption spectrum. Absolute CO$_2$ concentrations in the reactor were determined by comparing the integrated absorption of the asymmetric stretch band of carbon dioxide produced in the reactor and that of the known amount of CO$_2$. The calibration was performed using a mixture of 2.5% CO$_2$ in Air. Controlled amount of this mixture was diluted in Ar and flown through the reactor. The amount of CO$_2$ added to the mixture during calibration was in the same range as produced in the actual optical pumping experiments.

3. Results and discussion

Fig. 2 shows a typical CO$_2$ asymmetric stretch band (2349.15 cm$^{-1}$) absorption spectrum measured in the flow of chemical reaction products generated in the optically pumped CO–Ar–He mixture. The CO$_2$ number density calculated from the absorption spectra using the calibration procedure described in Section 2 is plotted in Fig. 3 as a function of helium partial pressure in the reactor at two different CO partial pressures, 9 Torr and 12 Torr. From Fig. 3, one can see that the carbon dioxide number density significantly decreases as the helium partial pressure increases. At both CO partial pressures, adding approximately 4 Torr of He to the mixture results in the CO$_2$ concentration reduction in the reaction products by about an order of magnitude, from $6 \times 10^{14}$ cm$^{-3}$ to $(2-4.0) \times 10^{13}$ cm$^{-3}$ s (see Fig. 3). On the other hand, CO$_2$ number density as a function of CO partial pressure remains nearly constant (see Fig. 4), varying by only 10–20% as the CO partial pressure is increased by a factor of 4, from 3 Torr to 12 Torr.

Fig. 5 shows the flow temperature in the laser-excited reaction zone inferred from the CO fundamental spectra, as discussed in Section 2. From Fig. 5, it can be seen that the temperature significantly increases with CO partial pressure, from 750 K to 1000 K, mainly due to stronger CO laser beam absorption, and weakly decreases with He.
partial pressure (by approximately 10% with the addition of 4 Torr of He). Summarizing the results of Figs. 3–5, one can see that adding helium to the CO–Ar mixture substantially reduces the resultant CO₂ concentration, although the flow temperature remains nearly constant. On the other hand, adding CO to the mixture does not affect the CO₂ concentration although in this case both the flow temperature and the reactant (CO) concentration increase. This behavior clearly demonstrates that CO₂ formation in the optically pumped cell is controlled by a non-thermal chemical reaction, with a non-Arrhenius rate coefficient dependence.

Fig. 6 shows CO vibrational distribution functions (VDFs) in optically pumped CO–Ar–He mixtures at different He and CO partial pressures, inferred from the first overtone CO spectra, as discussed in Section 2. Note that Fig. 6(a) plots relative (normalized) CO vibrational level populations at different He partial pressures, while Fig. 6(b) plots absolute CO vibrational level populations at different CO partial pressures. It can be seen that vibrational levels as high as \( v = 37 \) are detected. From Fig. 6(a), it is apparent that adding He to the CO–Ar mixture affects only high vibrational level populations \((v > 15)\), while the low level populations remain very nearly the same as without helium. The effect of high CO vibrational level depopulation by helium (helium titration) is due to rapid vibrational relaxation of CO in collisions with He atoms, and has been previously observed in optical pumping experiments [17–19]. On the other hand, Fig. 6(b) shows that although adding CO to the mixture does increase absolute populations of low vibrational levels, up to \( v = 15–20 \), the high level populations \((v > 25)\) remain nearly unchanged.

Comparing the results of Fig. 6 with the measurements of the CO₂ concentration, which decreases with helium partial pressure and does not change with CO partial pressure (see Figs. 3 and 4) suggests a straightforward conclusion: the CO₂ concentration in the reactor is primarily controlled by the high CO vibrational level populations, rather than by flow temperature or by CO partial pressure.

To infer the rate constant of the CO disproportionation reaction (reaction of Eq. (4)) from the results of measurements presented in Figs. 3–6, we have used a perfectly stirred reactor (PSR) approximation [25]. This approximation assumes that the chemical composition of the mixture at any point in the reactor is the same. Indeed, since the flow rate of the mixture through the reactor is very small \((24 \text{ cm}^3/\text{s})\), the flow residence time in the reactor is several seconds. The excitation of the vibrationally excited CO reactants, by absorption of the c.w. laser pump beam and subsequent Treanor up-pumping is extremely rapid, on a much shorter time scale than the residence time in the reactor; we have very rapid and spatially uniform excitation of the reactants. The residence time is sufficient to complete mixing of the reaction products before the flow exits the reactor, so that at steady state the CO₂ produced within the reaction zone is distributed uniformly over the entire volume of the reactor.

Using the PSR model, the rate constant of reaction of Eq. (4), \( k_f \), can be determined from the following equation:
\[
\frac{d[\text{CO}_2]}{dt} \cdot V_{\text{reactor}} = -[\text{CO}_2] \cdot F + k_t \cdot [\text{CO}] \cdot [\text{CO}] \cdot V_{\text{RZ}}, \tag{8}
\]

where \([\text{CO}_2]\) and \([\text{CO}]\) are the number densities [cm\(^{-3}\)] of carbon dioxide and of carbon monoxide in the reactor, \(F\) is the volumetric flow rate [cm\(^3\)/s]; \(V_{\text{RZ}}\) is the volume of the reaction zone (optically pumped plasma), and \(V_{\text{reactor}}\) is the total volume of the reactor. The volume of the reaction zone was determined from the visible emission from the vibrationally excited region, which is almost entirely due to the C\(_2\) Swan bands emission (the vibrationally excited region, which is almost entirely in the reaction zone (optically pumped plasma), and \(V_{\text{RZ}}\) is the total volume of the reactor. The volume of the reaction zone was determined from the visible emission from the vibrationally excited region, which is almost entirely due to the C\(_2\) Swan bands emission (the vibrationally excited region, which is almost entirely due to the C\(_2\) Swan bands emission (the vibrationally excited region, which is almost entirely due to the C\(_2\) Swan bands emission (the vibrationally excited region, which is almost entirely due to the C\(_2\) Swan bands emission). Electronically excited C\(_2\), with a radiative lifetime of 3.16 \(\mu\)s, is also formed in chemical reactions of the optically pumped CO. The short radiative lifetime precludes significant diffusion of electronically excited C\(_2\) out of the reaction volume, so that the size of the visible emission region is close to the volume of the vibrationally excited region. The emission region is a long slender cylinder approximately 10 cm length. The plasma diameter was also measured using a probe (a thin wire) inserted into the plasma. The probe was moved perpendicular to the plasma to find the positions where it clips the visible emission region from two opposite sides. The distance between these two positions turned out to be \(d = (1.74 \pm 0.1)\) mm. A very similar result, \(d = (1.67 \pm 0.08)\) mm, was obtained by photographing the plasma and the CaF\(_2\) window from a large distance and then comparing the size of the emission region with the diameter of the window. The emission volume remained approximately constant in all experiments reported here, although diminishing in radiative intensity with the addition of helium. These dimensions give a reaction volume \(V_{\text{RZ}} = (0.23 \pm 0.03)\) cm\(^3\).

Note that the reverse reaction of Eq. (4) is not included in the present analysis. Indeed, nascent C product of the Boudouard reaction is rapidly removed by a subsequent reaction with the most abundant reactive species in the mixture, carbon monoxide,

\[
\text{C} + \text{CO} + \text{M} \rightarrow \text{C}_2\text{O} + \text{M}, \tag{9}
\]

producing C\(_2\)O and other carbon suboxide products detected in previous CO optical pumping experiments [14,26,27]. Therefore, at steady state Eq. (8) gives:

\[
k_t = \frac{[\text{CO}_2] \cdot F}{[\text{CO}] \cdot [\text{CO}] \cdot V_{\text{RZ}}} \tag{10}
\]

Thus, the reaction rate constant predicted by the PSR model is proportional to the CO\(_2\) concentration in the reactor, and inversely proportional to the square of the CO concentration, which are both measured in the present experiments. Note that the rate constant given by Eq. (10) does not explicitly depend on the high CO vibrational level populations, which control the CO\(_2\) production rate in the optically pumped plasma (see Figs. 3,4 and 6 and the discussion above). Therefore, while Eq. (10) allows inference of the rate constant from the CO\(_2\) and CO concentration measurements, it cannot help determining the activation energy of the reaction of Eq. (4).

To infer the reaction activation energy from the present experimental results, we have used the statistical transition state theory [28,29], which assumes that two vibrationally excited CO molecules form a transition complex, with the total vibrational energy randomly distributed among all available vibrational modes of the complex. Then the overall rate constant of reaction of Eq. (4) can be expressed as follows:

\[
k^\text{rev}_t = \sum_{i=0}^{\text{max}} \sum_{j=0}^{\text{max}} k^\text{rev}_{tij}, \tag{11}
\]

where \(k^\text{rev}_{tij}\) is the state-specific rate constant,

\[
k^\text{rev}_{tij} = k_g \cdot \sqrt[6]{\frac{T}{300}} \cdot S \cdot A_{ij} \cdot f_v \cdot f_j \cdot \left(1 - \frac{E_a}{E_v + E_i}ight)^2 \cdot \left(\frac{\omega_{\text{CO}}}{\omega_{\text{CO}_2}}\right)^2 \tag{12}
\]

In Eq. (12), \(k_g = 3 \times 10^{-10}\) cm\(^3\) s\(^{-1}\) is the gas kinetic rate at room temperature, \(T\) is the temperature in the reaction zone (optically pumped plasma), \(S \leq 1\) is the steric factor, \(A_{ij}\) is the step function, \(A_{ij} = 1\) if \(E_v + E_i \geq E_a\) and \(A_{ij} = 0\) if \(E_v + E_i < E_a\), \(E_a\) and \(E_v\) are the vibrational energies of two CO molecules, \(\text{CO}(v)\) and \(\text{CO}(w)\), \(E_a\) is the reaction activation energy, \(f_v\) and \(f_j\) are normalized CO vibrational level populations, \(\omega_{\text{CO}} = 2214.24\) cm\(^{-1}\) and \(\omega_{\text{CO}_2} = 2226.85\) cm\(^{-1}\) are the vibrational quanta of CO and of CO\(_2\) asymmetric stretch mode, respectively. Basically, the state-specific rate coefficient given by Eq. (12) is a product of the gas kinetic collision frequency, the steric factor (i.e. the probability of the transition state complex formation in a collision), and the probability of the vibrational energy pooling into one of the CO vibrational modes (with the C–O bond breaking energy \(E_a\)). The steric factor in Eq. (12) accounts for the orientation of the colliding partners and is the probability that the collision geometry will favor the transition state complex formation. The double summation in Eq. (11) is over all CO vibrational levels populated at the present experimental conditions (\(v_{\text{max}} = 37\), see Fig. 6).

Since both the vibrational level populations and the temperature in the reaction zone are measured in the present experiments, Eqs. (10)–(12) allow evaluating the reaction activation energy, \(E_a\). Specifically, since the rate coefficient of the reaction is proportional to the CO\(_2\) concentration (see Eq. (10)), one can compare the behavior of the measured CO\(_2\) number density and of the rate constant predicted by Eqs. (11) and (12), both as functions of He partial pressure. For the comparison, we have used the CO vibrational level populations, \(f_v\) and \(f_j\), measured at different He partial pressures (see Fig. 6(a)) in Eq. (12), while the activation energy \(E_a\) in Eq. (12) was considered a parameter.

The results of the comparison for three different CO partial pressures are shown in Fig. 7(a–c). For each case, the results are plotted for two activation energies, \(E_a = 6\) eV (the activation energy for the reaction of Eq. (2)), and the one that provides the best fit with the experimentally
Partial pressure for two different activation energies; (a) 6 Torr CO, (b) 9 Torr CO, (c) 12 Torr CO in Ar, at 110 Torr total pressure.

From Fig. 7, it can be seen that the activation energy of $E_a = 6$ eV predicts a much slower CO$_2$ concentration reduction as a function of helium partial pressure, compared with the experiment. However, in all three cases, the activation energy near $E_a = 11$ eV (11.6 eV at $P_{co} = 6$ Torr, 11.9 eV at $P_{co} = 9$ Torr, and 11.4 eV at $P_{co} = 12$ Torr) provides very good agreement with the experiment. Such high value of the activation energy suggests that the gas-phase Boudouard reaction of Eq. (4) can occur only in collisions of two highly vibrationally excited CO molecules by pooling their vibrational energies together. Note that the inferred activation energy of $E_a = 11.6 \pm 0.3$ eV is close to the CO dissociation energy, 11.09 eV, which also suggests that the reaction proceeds via breaking one of the C-O bonds in the transition state complex.

Having determined the activation energy of the Boudouard reaction from the CO$_2$ concentration dependence on He partial pressure (see Fig. 7), we can now evaluate the value of the steric factor, $S$, in Eq. (12) by comparing the rate constants given by Eq. (10) ($k_f^{exp}$, from direct measurements of the CO and CO$_2$ concentrations) and by Eqs. (11) and (12) ($k_f^{cal}$, using the statistical theory at $S = 1$). The results are summarized in Table 1. The uncertainty in the $A_y$ is about factor of 2 and is mostly due to the uncertainty in determining the reaction region volume, $V_{RZ}$. The uncertainty in the $k_f^{cal}$ is primarily determined by the uncertainty in the activation energy determined from the data fits in Fig. 7, and is also about a factor of two. From Table 1, one can see that the values of the rate constants are of the order of $k_f \sim 10^{-17}$ cm$^3$/s, which is well below the estimates indirectly inferred from previous data of $\sim 10^{-15}$ cm/s [4]. It can also be seen that the two rate coefficients are in rather close agreement, within the accuracy of the present experimental results. From the comparison of the experimental and the calculated rate constants, it can be concluded that the steric factor for the rate constant of reaction of Eq. (4) is of the order of one, $S \sim 1$. Qualitatively, this suggests that nearly every collision between two CO molecules results in formation of a transition state complex, regardless of the collision geometry, and that at $E_v + E_w \gg E_a$ the reaction occurs on a near gas kinetic rate.

Fig. 8 shows relative contributions of state-specific reaction channels into the overall reaction rate coefficient, $k_f^{cal}/k_f$, as functions of vibrational quantum numbers, calculated from Eq. (12) using experimental VDFs at a CO partial pressure of 12 Torr. In Fig. 8, vibrational quantum numbers $w$ and $v$ are defined as follows:

$$\text{CO}(v) + \text{CO}(v + w) \rightarrow \text{CO}_2 + C.$$  \hfill (13)

Each curve in Fig. 8 corresponds to a different value of $w = 0, 2, 4, \ldots, 18$ (indicated in the plot), with $v$ being varied from $v = 0$ to $v = 37$. From Fig. 8, it can be seen that although vibrational levels as low as $v = 16$ can participate in the reaction of Eq. (4), the main contribution comes from the levels from $v = 22$ to $v = 32$. One can also see that
above the activation energy threshold, the state-specific rate coefficients plotted in Fig. 8 first increase because of the energy factor in Eq. (12), $1 - \left(\frac{E_v}{E_v + E_w}\right)^3$, and then gradually fall off because of the reduction of the vibrational level populations, $f_v$ and $f_w$, at higher vibrational levels. According to the statistical reaction rate model, the near resonant collisions (at small values of $w$) provide greater contribution to the overall reaction rate compared to collisions with a large vibrational energy difference between the collision partners (see Fig. 8).

As discussed in Section 1, there is no evidence of presence of electronically excited CO($a^3\Pi$) molecules in the optically pumped plasma at the present conditions. However, this electronic level might be excited by the same vibration-to-electronic ($V-E$) energy transfer mechanism, mediated by low-energy electrons, which results in production of CO($A^1\Pi$) molecules at similar experimental conditions [17,19,20]. Associative ionization in optically pumped CO–Ar–He mixtures occurs in collisions of highly vibrationally excited CO molecules [18,30]. Using Eq. (10), the lower bound CO($a^3\Pi$) number density necessary to produce the amount of CO$_2$ detected in the present experiments can be estimated as follows:

$$[\text{CO}(a^3\Pi)] = \frac{[\text{CO}_2] \cdot F}{k_r(a^3\Pi) \cdot [\text{CO}] \cdot V_{\text{eff}}},$$  \hspace{1cm} (14)

where $k_r(a^3\Pi) \sim 10^{-12} \text{ cm}^3/\text{s}$ is the rate constant of reaction of Eq. (2) [5,9], and other notations are the same as in Eq. (10). From Eq. (14), the minimum number density of CO($a^3\Pi$) molecules in the optically pumped mixture should be $\sim 5 \times 10^{11} \text{ cm}^{-3}$. Although such CO($a^3\Pi$) EQ concentrations are somewhat high, they are attainable in low-pressure CO glow discharges where CO($a^3\Pi$) molecules are produced by electron impact excitation. However, they are unlikely to be achieved in the optically pumped plasma, for two reasons. First, there is no direct electron impact excitation in the absence of electric field, and second, there is the rapid quenching mechanism of Eq. (7), which becomes dominant at high CO partial pressures. Also, the estimated minimum CO($a^3\Pi$) concentration would have to exceed the measured electron density in optically pumped CO–Ar plasmas, $n_e \sim 10^{10} \text{ cm}^{-3}$, by about two orders of magnitude [22,30]. Finally, the inferred reaction activation energy, about 11 eV, considerably exceeds the activation energy of the reaction of Eq. (2). All this indicates that the gas-phase Boudouard reaction in high-pressure optically pumped plasmas occurs by collisions of two highly vibrationally excited CO molecules in the ground electronic state (reaction of Eq. (4)). On the other hand, in low-pressure CO glow discharges the alternative channel with participation of CO($a^3\Pi$) molecules produced by electron impact is likely to be the dominant channel, because of low absolute populations of highly vibrationally excited CO molecules at low pressures.

### 4. Summary

The gas-phase Boudouard disproportionation reaction between two highly vibrationally excited CO molecules in the ground electronic state has been studied in optically pumped CO. The gas temperature and the CO vibrational level populations in the reaction region, as well as the CO$_2$ concentration in the reaction products have been measured using FTIR emission and absorption spectroscopy. The results demonstrate that CO$_2$ formation in the optically pumped reactor is controlled by a non-thermal chemical reaction, with a non-Arrhenius rate coefficient dependence. The CO$_2$ concentration in the reactor is primarily controlled by the high CO vibrational level populations, rather than by flow temperature or by CO partial pressure. The disproportionation reaction rate constant has been determined from the measured CO$_2$ and CO concentrations using the perfectly stirred reactor (PSR) approximation. The reaction activation energy, $11.6 \pm 0.3 \text{ eV}$ (close to the CO dissociation energy of 11.09 eV), was evaluated using the statistical transition state theory, by comparing the dependence of the measured CO$_2$ concentration and of the calculated reaction rate constant on helium partial pressure. This suggests that the gas-phase Boudouard reaction occurs in collisions of two highly vibrationally excited CO molecules by pooling their vibrational energies together. Finally, the reaction rate constants obtained from the experimental measurements and from the transition state theory are in good agreement. This suggests that nearly every collision between two CO molecules results in formation of a transition state complex (steric factor of $\sim 1$), and that the reaction occurs at a near gas kinetic rate if the combined vibrational energy of the reactants exceeds the activation energy. The disproportionation reaction rate constant measured at the present conditions is $k_r = (9 \pm 4) \times 10^{-18} \text{ cm}^3/\text{s}$. To the best of our knowledge, this is the first direct measurement of the rate constant of the gas phase Boudouard reaction in vibrationally excited, ground electronic state CO.
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