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# Diode laser absorption study of internal energies of CO<sub>2</sub> produced from catalytic CO oxidation

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Internal energy distributions for  $CO_2$  molecules produced in the catalytic oxidation of CO by  $O_2$  on polycrystalline platinum have been directly measured using a high resolution tunable diode laser (TDL) spectrometer. Absorption spectra have been collected for  $CO_2$  produced in a flow cell reactor for a wide range of temperatures and reactant ratios. Vibrational energies for  $CO_2$  produced under most reaction conditions are greater than would be expected from complete equilibration with the surface. The asymmetric stretching mode consistently exhibited a higher vibrational Boltzmann "temperature" than the bending or symmetric stretching modes. The level of vibrational excitation for all of the vibrational modes was sensitive to oxygen coverage, i.e., as either the  $O_2$ :CO reactant ratio or the surface temperature is increased, the vibrational temperature of the product  $CO_2$  increases significantly. © 1996 American Institute of Physics. [S0021-9606(96)02718-5]

## INTRODUCTION

The catalytic oxidation of carbon monoxide on platinum has been one of the most widely studied surface reactions since the time of Langmuir.<sup>1</sup> This reaction has important practical application in the removal of CO from the exhaust of combustion processes. However, the reaction also has generated considerable scientific interest as a simple model catalytic surface reaction.<sup>2</sup> As a result of the many studies carried out, a great deal is already known about the kinetics and mechanism of this reaction, but the dynamics of this reaction are somewhat less understood. It is our hope that by determining the internal energy distribution of the  $CO_2$  produced from this reaction under various conditions, a clearer picture of the surface reaction dynamics and of the transition state will emerge.

It has been well established that the oxidation of CO over noble metal catalysts occurs via a Langmuir– Hinshelwood (LH) mechanism,<sup>3</sup> where an adsorbed CO molecule reacts with an atomically adsorbed oxygen to form a carbon dioxide molecule as product. The CO<sub>2</sub> that is produced is only weakly bound to the surface [ $\Delta H \sim 5$  kcal/mol (Ref. 4)], and has been found to desorb with excess translational<sup>5–8</sup> and vibrational<sup>9–16</sup> energy. Molecular beam time-of-flight measurements show that CO<sub>2</sub> produced on a polycrystalline Pt surface desorbs with translational energy considerably higher than would be expected from complete equilibration with the surface. Angular distributions of product CO<sub>2</sub> were also found to be strongly peaked at the normal.<sup>5–8</sup>

Vibrational excitation has also been observed. In studies performed under conditions similar to that of the work presented here, Bernasek and Leone<sup>9</sup> and later Brown and Bernasek<sup>10</sup> used low resolution infrared chemiluminescence to detect vibrational excitation from CO<sub>2</sub> produced over a polycrystalline Pt gauze. Mantell *et al.*<sup>12,14,15</sup> also observed vibrational excitation at lower pressures ( $\sim 10^{-4}$  Torr) using FTIR spectroscopy. The vibrational spectrum produced by emission in the asymmetric stretch fundamental and the neighboring combination bands was detected at both low (8 cm<sup>-1</sup>) and high (0.012 cm<sup>-1</sup>) resolution. In high resolution FTIR experiments<sup>14,15</sup> individual rotational structures of several bands of CO<sub>2</sub> produced by CO oxidation on Pt foil were fully resolved. Each of these groups observed that the individual normal modes of product CO<sub>2</sub> exhibited energies that were above that expected for equilibration with the catalytic surface. Achieving a detailed picture of the excited gas phase CO<sub>2</sub> should allow one to gain insight into the dynamics of the surface reaction. In fact, measurements of normal mode vibrational energies have been used to guide trajectory calculations based on a proposed transition state for the reaction that is nearly linear and normal to the surface.<sup>17</sup>

Changes in oxygen coverages have been found to affect the energy of the desorbing  $CO_2$ . Ertl and co-workers<sup>7,18</sup> have seen sharpening of the desorption angular distribution with increasing oxygen coverage on Pt (111) surfaces. Mantell *et al.*,<sup>12</sup> using low resolution time resolved IR spectroscopy to track the vibrational spectrum of  $CO_2$  produced from polycrystalline Pt foil, observed that the vibrational temperature increased with increasing oxygen coverage. In high resolution IR emission studies for the reaction on Pd foil<sup>15</sup> an increase in  $O_2$ :CO reactant ratio from 1:1 to 2:1 resulted in a significant increase in vibrational energy for all vibrational modes.

In the present study we use a tunable diode laser (TDL) to obtain the absorption spectrum of  $CO_2$  produced in a flow cell reactor. Due to the high resolution of the TDL spectrometer (0.0007 cm<sup>-1</sup>), single rotational transitions can easily be resolved and populations of individual states can accurately be determined. Flynn and co-workers<sup>19–24</sup> have demonstrated in collisional energy transfer experiments, that diode laser absorption spectroscopy is well suited for measuring vibrational energy distribution in  $CO_2$ . The relative population of any state can be determined, including the ground state (which cannot be probed with emission techniques) and "IR



FIG. 1. Schematic diagram of experimental apparatus.

inactive" symmetric stretching states, by tuning the laser to a transition of the following type:

$$v_1 v_2^l v_3; J + h \nu (4.3 \ \mu m) \rightarrow v_1 v_2 l (v_3 + 1); J \pm 1.$$
 (1)

 $v_1$  is the quantum number for the symmetric stretch mode,  $v_2$  is the bending mode,  $v_3$  is the asymmetric mode, and *J* is the rotational quantum number. *l* is the angular momentum associated with the doubly degenerate bending motion. Due to the large oscillator strength of the asymmetric stretch, all such transitions are allowed. The relative populations for states in each of the vibrational modes are used to determine individual Boltzmann temperatures which allows for energy deposition comparisons between the modes.

In the work reported here, we use high resolution absorption spectroscopy to probe the internal energy of  $CO_2$ produced by CO oxidation on polycrystalline Pt in a flow reactor. To date almost all of the work in this area has used emission techniques to probe the vibrational and rotational energy of the desorbing  $CO_2$ . By using diode laser spectroscopy, we can probe the ground state levels as well as obtain a much higher resolution spectrum. We also report a significant increase in vibrational energy as the  $O_2/CO$  reactant ratio increases.

#### EXPERIMENT

The flow reactor/diode laser spectrometer is shown schematically in Fig. 1. The flow cell is connected to a mass spectrometer chamber through a capillary placed in the center of the flow tube. This allows for simultaneous time resolved monitoring of the reactant and product gases while supporting the pressure difference between the reactor cell (1.7 Torr) and the mass spectrometer chamber ( $\sim 10^{-6}$  Torr). A 60 L/s mechanical pump provides a linear flow of 1800 cm/s for a 1.7 Torr stream of high purity Argon. Electronic mass flow meters are used in each gas line to allow accurate measurement and control of reactant flow rates. The ultra high purity CO and  $O_2$  were premixed behind a piezoelectric valve in order to insure consistent composition of the gases as they entered the established carrier gas flow. The platinum surface is a  $3.5 \times 2.0$  cm piece of 100 mesh high purity polycrystalline gauze. It is mounted on a removable and adjustable sample holder that allows for easy movement of the surface in relation to the laser probe. The surface is heated resistively and its temperature is determined by a Chromel–Alumel thermocouple spot welded to the center of the gauze.

The striped TDL is a standard Laser Photonics element tunable over the spectral region of the CO<sub>2</sub> asymmetric stretch, 2275–2340 cm<sup>-1</sup>, in a series of modes ranging from 0.8 to 2.5 cm<sup>-1</sup> in width. The resolution of the spectrometer is better than 0.0007  $\text{cm}^{-1}$ . The divergent output of the laser is collimated by an f/1 CaF2 lens and directed through the CaF<sub>2</sub> windows of the flow cell where the beam was measured to be 5-6 mm in diameter where it passed by the gauze. In most of the data presented here, the upstream edge of the collimated laser beam was obscured by the side of the gauze insuring minimum time for gas phase CO2 molecules produced at the gauze to collisionally relax. The infrared signal is detected by a 3 mm diam 77 K InSb photovoltaic detector and preamplifier. The signal is amplified, then digitized and sent to a PC for data collection and manipulation. The same computer, through a Laser Photonics control module model L5820, controls the output of the laser during each sweep in a typical 1000 sweep data set. Each data set covers a tuning range of 3.2-4.0 cm<sup>-1</sup> including 2-3 distinct lon-



FIG. 2. CO conversion % as a function of temperature and reactant ratio. The three O2:CO reaction ratios (sccm) are 7:1 (350:50), 4:1 (200:50), 1:1 (50:50).

gitudinal modes and requires roughly 6 min collection time.

When working with the TDL a frequency calibration is needed within each mode. Absolute frequency differences between transitions were determined by using a solid Ge étalon (free spectral range of 0.0482 cm<sup>-1</sup>). Each range was then calibrated by comparing the collected spectrum with line positions and intensities for CO<sub>2</sub> thoroughly tabulated in the HITRAN (Ref. 25) database. The sensitivity of the spectrometer allows transitions from the lowest 19 vibrational levels of CO<sub>2</sub> to be measured with acceptable confidence. In order to insure that the TDL was lasing in a single longitudinal mode a monochrometer was used in the initial calibration. Since the monochrometer was not used during data collection, periodic checks of the TDL were performed to make sure that multi-mode behavior did not arise from laser degradation over time.

Prior to all reaction studies the Platinum gauze was heated to 1100 K in a flow of 1.0 Torr of argon and 200 sccm (standard cubic centimeters per minute)  $O_2$  for 45 min in an effort to maintain consistent surface conditions. Checks of the steady state reaction for a given gauze temperature and reactant ratio using the mass spectrometer showed constant levels of CO<sub>2</sub> production over a 6+ h period. This insured all data sets taken in series probed the same density of product CO<sub>2</sub> molecules. Note that it was not imperative in these experiments to know absolutely how much CO<sub>2</sub> was being detected by the laser, it was only necessary to know that the effective pressure was constant.

## RESULTS

Figure 2 shows mass spectrometer measurements of the amount of  $CO_2$  produced during the reaction as a function of temperature for three different reactant ratios. It has been

established<sup>26</sup> that the surface concentrations of adsorbates varies considerably with respect to temperature and reactant ratio. A curve similar to Fig. 2 was obtained using the diode laser tuned to a single transition of the ground state (P20) and monitoring the intensity as a function of temperature. After correcting for changes in rotational temperature the only difference was a steeper drop in production at the higher temperatures. This is likely to be a result of the nonuniform resistive heating of the Pt gauze. The CO conversion % is obtained by monitoring the CO and CO<sub>2</sub> mass spectrometer signals simultaneously and normalizing this conversion ratio to the cross section of the active region of the gauze.

The kinetics of the reaction vary substantially over the temperature range in Fig. 2. At temperatures lower than the temperature of maximum conversion %,  $T_{\rm max}$ , the reaction is negative order in CO pressure and positive order in O<sub>2</sub> pressure. At  $T > T_{max}$  the reaction is seen to be positive order in CO pressure and nearly zeroth order in O<sub>2</sub> pressure. At the lower temperatures, it has been well established<sup>3</sup> that the observed kinetics are a result of the surface being covered predominantly by CO. Adsorbed CO inhibits the dissociative adsorption of oxygen, so the reaction is limited by CO desorption. As the CO molecule desorbs, sites are open for oxygen adsorption. Once an oxygen atom is on the surface it immediately combines with an adsorbed CO and is converted to product. As the temperature is increased, more CO can desorb and the CO<sub>2</sub> production rate increases. Above  $T_{\text{max}}$  CO coverage on a surface has decreased and O<sub>2</sub> coverage is increased, so that the reaction is limited by CO that adsorbs and reacts before desorbing. Since oxygen coverage does not inhibit CO adsorption, the oxygen pressure effect is negligible.

Absorption spectra were collected for CO<sub>2</sub> produced



FIG. 3. A portion of a typical absorption spectrum. Collected for the CO oxidation reaction at 900 K and 1:1  $O_2$ :CO reactant ratio. Peak assignments: 1) 100(2) P48; 2) 001(1) P45; 3) 110(2) P36; 4) 120(1) P21; 5) 120(2) P23; 6) 021(1) P19; 7) 010(1) P56; 8) 030(1) P32; 9) 210(2) P12; 10) 110(1) P34; 11) 210(3) P12; 12) 011(1) P32; 13) 200(1) P22; 14) "CO" 0(1) R47; 15) 020(1) P44; 16) 040(1) P18; 17) 120(1) P20; 18) 100(1) P46; 19) 021(1) P18; 20) 120(2) P22; 21) 110(2) P35; 22) 200(2) P26; 23) 030(1) P31; 24) 000(1) P66; 25) 010(1) P55.

from CO oxidation by O2 over Pt under various reaction conditions. In some cases the surface temperature was changed while the reactant ratio remained constant and vice versa. A portion of a typical spectrum is shown in Fig. 3. This scan was taken at a 1:1 O<sub>2</sub>:CO ratio and 900 K surface temperature. It was obtained by sweep integration for 1000 iterations and subsequent division by the background laser intensity in the absence of  $CO_2$  in the flow. The  $v_1$ ,  $v_2$ ,  $v_3$ , (r) notation follows that of Rothman *et al.*<sup>27</sup> As mentioned above,  $v_1$  is the symmetric stretch quantum number,  $v_2$  is the bending quantum number, and  $v_3$  is the asymmetric stretch quantum number. The symbol r represents the level in the various fermi resonating groups. In this scheme all bands in a fermi resonating group have the same quantum numbers and the value of r decreases with increasing band energy. The angular momentum associated with the bending motion, typically represented as l, is always equal to  $v_2$  in this notation and will be omitted.

Normalized intensities from the spectra were used to determine state populations relative to 296 K by use of Eq. (2),

$$\ln \frac{I_v}{I_0} = S_{vj}^0 \frac{f_v f_j}{f_v^0 f_j^0} \,\delta_{(v-v_0)} lN.$$
<sup>(2)</sup>

In this case,  $S_{vj}^0$  is the line strength at 296 K from the HITRAN database,  $f_v$  and  $f_j$  are the Boltzmann distributions for the vibrational and rotational levels being probed,  $f_v^0$  and  $f_j^0$  are Boltzmann distributions at 296 K,  $\mathcal{X}(v-v_0)$  is the Doppler line shape, l is the path length, and N is the molecular density. A rotational population relative to that at 296 K,  $Y_R$ , is obtained from Eq. (3) for each transition at its line center,  $v_0$ ,

$$Y_{R} = \ln \frac{I_{N}v_{0}}{S_{vj}^{0}} = \frac{E_{V}}{k} \left(\frac{1}{T_{0}} - \frac{1}{T_{V}}\right) + \frac{E_{J}}{k} \left(\frac{1}{T_{0}} - \frac{1}{T_{J}}\right) + \ln \left[\frac{Q_{vj}^{0}}{Q_{vj}} \,\delta_{(v_{0})} lN\right].$$
(3)

In Eq. (3),  $I_N$  is the normalized intensity,  $E_V$  and  $E_J$  are the vibrational and rotational energies,  $T_V$  and  $T_J$  are the Boltzmann temperatures to be determined,  $Q_{vj}$  is the vibrational and rotational partition function, and  $\delta(v_0)$  is the Doppler line shape at  $v_0$  with  $v_0$  included in the term  $Y_R$ . We can obtain a Boltzmann plot of the relative rotational populations for each vibrational band. Figure 4 shows results for four bands of varying energy. All of the bands exhibited the same rotational temperature for a given set of reaction conditions. This rotational equilibration is expected given the number of collisions between the product  $CO_2$  and the Ar carrier gas (as will be discussed below). If we further assume that there is equilibration within a given vibrational mode we can extract vibrational Boltzmann temperatures for each mode individually. Rearranging Eq. (2) to give  $Y_V$ , the relative vibrational population, we get Eq. (4),

$$Y_{V} = \ln \frac{I_{N}v_{0}}{S_{vj}^{0}} - \frac{BJ(J+1)}{k} \left(\frac{1}{T_{0}} - \frac{1}{T_{J}}\right)$$
$$= \frac{E_{V}}{k} \left(\frac{1}{T_{0}} - \frac{1}{T_{V}}\right) + C, \qquad (4)$$

where *C* contains the constant terms from Eq. (2). An average value of  $Y_V$  is calculated for all rotational transitions detected within each band. This average value  $\pm$  one stan-



FIG. 4. Rotational population distributions for several different vibrational bands of CO2. All of the data were taken for the reaction at 900 K and 3:1 O2:CO ratio. The best straight line through the data gives a measure of a Boltzmann rotational temperature. All levels, regardless of vibrational energy, exhibited the same rotational temperature ( $\sim 800$  K).

dard deviation is plotted vs  $E_V$  for bands within a given vibrational mode and the best straight line through these points has a slope that is proportional to the vibrational Boltzmann temperature,  $T_V$ .

The product  $CO_2$  in these experiments undergoes a significant number of collisions with the three other gases in the flow (Ar, CO, and  $O_2$ ). Most of the collisions occur with the Ar carrier gas. It was estimated that under experimental conditions (1.7 Torr) a  $CO_2$  molecule has 1100 Ar collisions during the time it takes to travel 2.5 mm downstream from the Pt gauze. The distance, 2.5 mm, conservatively estimates the average distance a molecule travels into the laser beam before it is detected. Using similar analysis it was estimated that product CO<sub>2</sub> would have 35–40 reactant gas collisions for a flux of 100 sccm in the flow. The total number of collisions should ensure that the rotational state distributions are equilibrated. Based on collisional energy transfer rates,<sup>28</sup> each vibrational mode should also be described well by a Boltzmann distribution. However, the various modes should not necessarily be equilibrated with one another. The fermi resonant bending and symmetric stretching modes should equilibrate relatively quickly with each other and any subsequent vibrational relaxation could affect both equally.<sup>29</sup> In order to mix with the Fermi resonant modes, the asymmetric stretching mode requires nonresonant energy transfer which is a much slower process. In the data presented here the  $v_1$ and  $v_2$  modes consistently track each other in energy, but the  $v_3$  mode can be described by a distinct temperature.

In all of the experiments performed, the CO<sub>2</sub> that was produced exhibited vibrational temperatures in excess of those expected from full accommodation with the surface. The excess temperature was found to depend on reactant ratio and surface temperature. It should be noted that the term "temperature" as used in this study is not necessarily a true temperature. It is a parameter used to describe the observed population distribution of the rovibrational states, assuming them to have a Boltzmann distribution. Therefore the "temperature" is the parameter to which the observed populations are fit. The population distribution of the true nascent  $CO_2$  molecules may or may not be Boltzmann, but under the experimental conditions in this study all of the observed populations fit a straight line in a Boltzmann-type plot.

A plot of  $Y_V$  vs  $E_V$  of all the levels detected for a 7:1 O2:CO ratio is shown in Fig. 5. The straight line is drawn through all of the levels that correspond to either the bending or symmetric stretching modes. The vibrational temperature determined from the slope of this line is  $1130\pm15$  K. This particular value is for the combination of bending and symmetric stretching levels, however, as it is not always clear that these modes are equilibrated with each other, different temperatures will be determined for each mode. The temperature of the bending mode,  $T_B$ , is determined from the relative populations of the 000, 010, 020, 030, and 040 levels. The symmetric mode temperature,  $T_S$ , is determined from the relative populations of the 000, 100(1), 100(2),200(1), and 200(2) levels. The temperature of the asymmetric mode,  $T_{AS}$ , is determined from the relative populations of both the 000 and 001 levels and the 010 and 011 levels. The slopes of these lines between each of these sets of levels consistently gives the same vibrational temperature within the error for the asymmetric stretch ( $\pm 55$  K).

Figure 6 shows the temperature for each normal mode as a function of reactant ratio for the CO oxidation reaction at 900 K. All of the vibrational temperatures increase with increasing O<sub>2</sub>/CO ratios.  $T_{AS}$  is consistently greater than  $T_B$ and  $T_S$ , and all of the temperatures are above the surface temperature. The rotational temperatures calculated at each of the reactant ratios are 850 K for 7:1, 830 K for 4:1, 815 K for 1.5:1, 800 K for 1:1, and 790 K for 0.5:1. All of the rotational temperatures are below surface temperature,  $T_{\rm Pt}$ , but follow the same trend as the vibrational temperatures. These rotational temperatures are determined by the overall flow temperatures. For a given gauze temperature, the additional O<sub>2</sub> increases the flow temperature as measured by a second thermocouple suspended in the stream.

In Fig. 7 vibrational and rotational temperatures are plotted vs surface temperature for a 1:1 (150:150 sccm) reactant ratio. Again, the asymmetric mode consistently has a greater temperature than the two Fermi resonant modes. The solid straight line in Fig. 7 corresponds to  $T_{Pt} = T_{CO_2}$  which would be expected if the CO<sub>2</sub> was completely accommodated with the surface before desorbing. The rotational temperatures are again lower than  $T_{\rm Pt}$  and they increase at a rate slower than both  $T_V$  and  $T_{Pt}$ .



FIG. 5. A plot of relative population versus  $E_V$  of all the levels detected for a 7:1 O<sub>2</sub>:CO ratio. The straight line is drawn through all of the levels that correspond to either the bending or symmetric stretching modes, that is all except the 001 and 011 levels.



FIG. 6. Vibrational temperature of each normal mode of  $CO_2$  as a function of reactant gas ratio in the flow tube for the CO oxidation reaction at 900 K.



FIG. 7. Vibrational and rotational temperatures of product  $CO_2$  as a function of surface temperature for a 1:1  $O_2$ :CO reactant gas ratio. The solid straight line corresponds to the temperature expected from complete accommodation of the  $CO_2$  with the surface.

### DISCUSSION

In the above experiments, we observed an increase in product CO<sub>2</sub> vibrational energy with increasing O<sub>2</sub>:CO reactant ratio. In order to discuss the effect of reactant gas ratio on the product vibrational energy, we first need to know how the reactant gas ratio affects the surface during the reaction. Based simply on considerations of flux of reactant molecules to the surface, an increase in oxygen coverage,  $\theta_{O}$ , is expected at the higher O<sub>2</sub>:CO ratios. There are other factors that affect the surface coverages, however. As seen in Fig. 2, at higher oxygen ratios the CO conversion percentage increases and  $T_{\text{max}}$  decreases. Oxygen coverages can be estimated for the Pt surface at 900 K using Eq. (5),<sup>30</sup>

$$\theta_{\rm O} = \theta_{\rm max} [1 - X_{\rm CO} / (2S_{\rm O}R)], \tag{5}$$

where  $\theta_{\text{max}}$  corresponds to 0.5 ML,  $X_{\text{CO}}$  is the fractional CO conversion from Fig. 2,  $S_0$  is the sticking coefficient for oxygen which was taken to be 0.1,<sup>31</sup> and *R* is the O<sub>2</sub>:CO ratio. This relation assumes that O<sub>2</sub> adsorption is first order in the concentration of vacant sites. Since CO coverage should be very low at 900 K, any CO inhibition effect on O<sub>2</sub> adsorption can be neglected. At this surface temperature and O<sub>2</sub> flux, oxygen desorption is negligible. The estimated coverages at the reactant ratios in Fig. 2 are 0.4 at 7:1, 0.3 at 4:1, and 0.1 at 1:1. This estimate is only valid for conditions where CO coverage is very low, i.e.,  $T > T_{\text{max}}$ . These values are only rough estimates of coverage, but do suggest a significant increase in  $\theta_0$  with increasing O<sub>2</sub>:CO ratio.

It is important to consider how the observed increase in vibrational energy depends on surface coverage. The internal excitation of the CO<sub>2</sub> is thought to be related to the activation barrier for the surface reaction.<sup>18</sup> The product CO<sub>2</sub> that desorbs retains some of the energy that is necessary to surmount the barrier. The activation energy associated with this barrier,  $E_{\rm LH}$ , is known to depend on oxygen coverage. In the low coverage limit,  $E_{\rm LH}$  is 25 kcal/mol and falls to 12 kcal/mol at higher coverages.<sup>7</sup> A one dimensional reaction coordinate for this reaction is shown in Fig. 8.<sup>18</sup> Although it is an oversimplification of the actual situation, this diagram has been used previously and is useful when discussing reaction energetics. The depth of the prebarrier well is primarily determined by the adsorption energies of the CO and O reactant species. These energies are known to decrease with increasing coverage32 which is thought to contribute to the above mentioned decrease in  $E_{\rm LH}$ . However, when discussing the energy of the desorbing product CO<sub>2</sub> molecule, the important value is  $E_n$ , the total energy available to the product. Therefore any changes in vibrational energy that originate from changes in  $E_n$  would involve a change in the potential energy and nature of the transition state.

As mentioned previously,<sup>17</sup> a transition state has been proposed that involves a nearly linear and perpendicular  $CO_2^*$  species. Such a model requires a CO molecule to move atop an adsorbed oxygen atom. In this case  $E_{LH}$  would correspond to the energy required for this motion. The transition state would still have a relatively strong M=O bond. Therefore any changes in the adsorption energy of oxygen, should

FIG. 8. A one dimensional potential energy diagram for the oxidation of CO on platinum. The numerical values refer to the limit of low coverage.

also change the potential energy of the transition state. The adsorption energy of oxygen is found to decrease at higher coverage due to repulsive interactions.<sup>32</sup> These same interactions may also affect the transition state. An increase in the energy of  $CO_2^*$  would increase the energy available to the desorbing  $CO_2$  molecule, which would lead to an increase in internal energy.

An increase in vibrational energy may also be attributed to a reduction in the fraction of available energy transferred to the surface at higher coverages. Segner et al., in measuring the translational energy of the desorbing CO2 in molecular beam experiments, found that the angular distribution could be described by a two channel model.<sup>7</sup> A fraction of the product desorbed in thermal equilibrium with the surface, while the remainder showed a substantial excess of translational energy, fitting a  $\cos^7 \gamma$  distribution. The fraction accommodated,  $\alpha$ , was found to decrease with increasing oxygen coverage. The shape of the angular distribution was always consistent with a cos  $\gamma$  fraction and a cos<sup>7</sup>  $\gamma$  fraction, independent of coverage. This indicates that the observed changes in  $\alpha$  arose from variations in the amount of energy transferred prior to desorption. In this interpretation, the increase in  $\alpha$  with decreasing oxygen coverage implies that energy transfer proceeds more completely on clean platinum than in the presence of adsorbed oxygen.

If this change in energy transfer applies to vibrational energy as well, then one would expect to see higher vibrational temperatures at the higher coverages, as we observed. In fact, in a low collision environment one might expect to fit

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the observed state populations to two distinct temperatures, one for accommodated and the other for hot CO<sub>2</sub>. In the present work no evidence of this two temperature behavior was observed. However, given the number of gas phase collisions under these flow conditions, one might expect to see an equilibrated population distribution. Additionally, the process of vibrational energy transfer between adsorbate and surface is likely more complicated than that for translational energy transfer. This may result in an averaging effect where all molecules are partially equilibrated and exhibit a single temperature. The extent to which the equilibration occurs would still be sensitive to oxygen coverage. At any rate, the observed trends in vibrational excitation as a function of coverage are consistent with this model.

Under most conditions in this study the asymmetric stretching mode,  $v_3$ , exhibited higher temperatures than the other two normal modes. The same result was seen under similar conditions for the low resolution chemiluminescence study performed in this laboratory.9 This preferential channeling of energy into the  $v_3$  mode suggests that the motion along the reaction coordinate involves a significant amount of asymmetric stretching. That is, as the reaction proceeds, the C=O bond in the carbon monoxide molecule lengthens as the newly forming C=O bond shortens. This motion along with a nearly linear transition state could lead to the higher temperature observed for the asymmetric stretching mode.

In the high resolution emission study by Coulston and Haller,<sup>15</sup> they report no preferential partitioning of energy between the vibrational modes for CO<sub>2</sub> produced on Pt at 814 K. The temperatures they obtained are 1500±100 K,  $1600\pm50$  K, and  $1550\pm140$  K for the  $v_1, v_2$ , and  $v_3$  modes, respectively. In contrast, for the oxidation reaction on Pd, they detect a higher apparent temperature for the symmetric stretch levels. A major difference between these studies and the present work is the pressure range in which the reaction is carried out. In the chemiluminescence study the authors estimated that 93% of the CO2 molecules undergo no CO<sub>2</sub>-CO<sub>2</sub> collisions and 63% undergo no more than one CO<sub>2</sub>-reactant gas collisions before being detected. Under such low collision conditions only a very small amount of energy loss would be expected. In fact Coulston and Haller observed very little mixing of the Fermi resonant levels which proceeds at a rate that is nearly gas kinetic.

In light of these results one might ask if the energy distribution observed in the present study is a result of different collisional deactivation rates for each mode. If this were the case, whatever initial difference (if any) in energy deposition into the modes would be obscured by subsequent energy loss by gas phase collisions with the other substituents of the flow. One need be concerned only with collisions which remove energy from the nascent CO<sub>2</sub>, not merely repartition it within a vibrational mode. Since the  $v_1$  and  $v_2$  modes are strongly coupled due to the very fast fermi resonant vibrational to vibrational, V-V, energy transfer, one can assume that they relax together. Therefore, in order to track energy leakage from the normal modes, one can look at the deactivation rates of the (010) level and (001) level of CO<sub>2</sub>. Significant energy loss could potentially result from collisions with the Ar carrier gas as well as the unreacted CO and O<sub>2</sub> reactant gases.

Under our experimental conditions, the majority of  $CO_2$ collisions are with Ar atoms. The deactivation of CO<sub>2</sub> by Ar occurs via vibrational to rotational and translational (V-R,T) energy transfer. In the case of CO<sub>2</sub> (001) deactivation by argon, the process most likely involved is shown in Eq. (6),

$$CO_2(001) + Ar \leftrightarrow CO_2(nm0) + Ar + \sim 270 \text{ cm}^{-1}.$$
 (6)

In the case of  $CO_2$  (010), the molecule relaxes to the ground state by the process shown in Eq. (7),

$$CO_2(010) + Ar \leftrightarrow CO_2(000) + Ar + 667 \text{ cm}^{-1}.$$
 (7)

Published results indicate that the vibrational deactivation rate for process 7 (Ref. 33) is four times the deactivation rate for process 6 (Ref. 34) at 800 K. This could explain the observed difference in vibrational mode temperatures. The vibrational relaxation is clearly not complete since all vibrational temperatures are above that of the predominantly argon flow stream temperature ( $\sim$ 800 K). However relaxation may be more complete in the  $(v_1 + v_2)$  manifold than the  $v_3$ manifold.

In addition to CO<sub>2</sub>—Ar collisions, CO<sub>2</sub>—CO collisions might also play a role in the relaxation of the nascent carbon dioxide. However this would not cause the higher temperatures that were observed for the  $v_3$  mode, because CO is known to deactivate the  $CO_2$  (001) level much more efficiently than the  $CO_2$  (010) level. The reason for this efficient deactivation of the  $v_3$  mode is the near resonant V-V energy transfer process shown in Eq. (8),

$$CO_2(001) + CO(v = 0) \leftrightarrow CO_2(000) + CO(v = 1)$$
  
+ 208 cm<sup>-1</sup>. (8)

At 800 K, the deactivation probability for the process above is  $\sim 2 \times 10^{-3}$  or 1 in 500 collisions.<sup>35</sup> Given the estimated CO collisions a CO<sub>2</sub> molecule undergoes for our flow conditions, there may be some energy loss, but that would disproportionately affect the  $v_3$  mode. If this were the case then the preferential energy partitioning into the  $v_3$  mode would be more pronounced for the nascent  $CO_2$  molecule.

Collisional relaxation of CO<sub>2</sub> by O<sub>2</sub> should not be significant under the flow conditions of this study. The process for deactivation by  $O_2$  is thought to be V-R,T because the deactivation probability is very close to that of argon.<sup>36</sup> Whatever the process, the data in this study indicates an increase in vibrational temperature for each of the modes as the amount of  $O_2$  in the flow (and correspondingly  $O_2$ -CO<sub>2</sub> collisions) increases from 75 to 500 sccm. Therefore, under these collision conditions, any additional deactivation of the nascent  $CO_2$  by  $O_2$  is either negligible or small compared to the increased excitation.

Because of this collisional relaxation, the level of excitation reported in this study can be considered only a lower limit of the actual nascent excitation. In fact higher vibrational temperatures have been reported in other laboratories

as well as in this one. The work previously performed in this lab under similar conditions detected infrared chemiluminescence at low resolution as a way of determining vibrational excitation. However, in order to obtain meaningful vibrational temperatures from the observed intensities, a reference intensity from a known temperature and pressure of  $CO_2$  is needed. The emission signal from a flow of high purity CO<sub>2</sub> in the tube was used for this intensity calibration. That is, the normalized intensity from CO<sub>2</sub> produced from reaction at a given temperature was compared to the intensity from the high purity CO<sub>2</sub> passing over the Pt gauze at the same temperature. It was assumed that the high purity CO<sub>2</sub> equilibrated with the surface and had vibrational temperature equal to the gauze temperature. In using the diode laser spectrometer, which does not require an intensity calibration, it was found that the vibrational temperature of the high purity  $CO_2$ in the flow was significantly lower than the temperature of the gauze. This over estimate of the reference signal resulted in an over estimate of vibrational temperatures for these previous studies.

In order to eliminate the confusion which arises from collisional relaxation, this experiment should be performed at lower pressures ( $\sim 10^{-4}$  Torr). This would require an increase in sensitivity for the diode laser spectrometer used in these studies. At present the relatively simple apparatus involves a single pass absorption and sweep integration of the laser intensity in order to collect the spectra. At lower pressures, where additional gas phase collisions would not be as significant, one could employ a multipass cell. In addition, both lock-in detection and longer sampling times could be used to improve the signal to noise ratio in low pressure experiments. Better sensitivity is achievable and we plan to perform this experiment in a molecular beam scattering apparatus in order to eliminate the confusion associated with collisional relaxation and intermode equilibration.

By performing diode laser absorption spectroscopy in a low collision environment, one could obtain the nascent energy distribution not only between the vibrational modes, but also within each mode. In the case of photofragmentation of pyruvic acid,<sup>37</sup> 97% of the CO<sub>2</sub> produced is observed to be directly formed in the ground vibrational state. The remaining molecules exhibit vibrational temperatures greater than 1800 K. These data indicate that there are two separate channels for CO<sub>2</sub> production from this photofragmentation. Since absorption spectroscopy is sensitive to the ground state, it can be employed to determine if a similar situation is occurring within the vibrational modes of CO<sub>2</sub> produced from CO oxidation reactions.

We are presently using this apparatus to study the internal energy distributions of the products of other catalytic oxidation systems. These systems include CO oxidation by NO, as well as hydrocarbon (ethylene and methanol) oxidation by  $O_2$ . In each of these systems the internal energy distributions of the product  $CO_2$  can be probed in order to compare and contrast to what we have reported here. This can give us information on both the possible mechanistic similarities and the effects of additional nonreactant surface species on the dynamics of the  $CO_2$  formation. Additionally, with the proper choice of laser, the internal energy distributions of other reaction products (i.e., CO,  $H_2O$ , and  $N_2O$ ) may be determined.

### CONCLUSION

In the above work a technique is described that combines the high resolution and good sensitivity of diode laser absorption spectroscopy with the flexibility and high signal levels of a flow reactor. This technique allows one to obtain a highly detailed picture of the vibrational and rotational energy distribution of CO<sub>2</sub> produced on a catalytic surface. Diode laser absorption spectroscopy has significant advantages over the chemiluminescence emission spectroscopy used to date by several groups to study the CO oxidation reaction. This absorption technique has better resolution than the emission FTIR experiments and provides information on the ground state population which is inaccessible by emission spectroscopy. This combination of flow reactor and laser spectrometer could be used to study other surface reaction systems in order to investigate if similar nonequilibrium energy distributions exist as has been seen in the CO oxidation reaction.

Carbon dioxide produced from catalytic oxidation of CO exhibits vibrational energies greater than would be expected from complete equilibration with the Pt surface. Vibrational temperatures for all of the normal modes are greater than the surface temperature. However, the asymmetric stretching mode is vibrationally "hotter" than the other two normal modes. This apparent preferential channeling of energy suggests that the motion along the reaction coordinate involves a significant amount of asymmetric stretching.

We have observed an increase in vibrational energy with increasing oxygen coverage, because of the coverage dependence of the reaction potential energy surface. Increased oxygen coverage raises the potential energy of the transition state. This provides additional energy available to the desorbing  $CO_2$  resulting in vibrational excitation. Determining the product energy distributions in heterogeneous reactions allows one to gain insight into the dynamics of the surface reactions.

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