Angle-Resolved Measurements of Rotational and Vibrational Energies of Product CO₂ in Catalytic CO Oxidation on Pd Surfaces

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Measurements of rotational and vibrational energies of desorbing products in chemical reactions provide useful information on dynamical processes of bond formation and bond rupture and also on structures of transition states. In order to obtain structural information, dependence of these energies on the desorption angle of products should be studied. However, such angle-resolved (AR) measurements of internal energies in thermal surface reactions have long time been lacking due to difficulty of experiments. Recently, measurements of internal energies of AR product CO₂ in CO oxidation on Pd surfaces have become possible by detecting extremely weak infrared chemiluminescence from desorbing CO₂. Rotational and vibrational energies change depending on polar and azimuth angles and also on surface structures, providing new insights into structures of transition states and energy partition dynamics. In this review, recent progress in the above AR measurements is described. [DOI: 10.1380/ejssnt.2008.180]

Keywords: Catalysis; Chemiluminescence; Oxidation; Palladium; Carbon monoxide; Carbon dioxide; Oxygen; Single crystal surfaces

I. INTRODUCTION

Activity in surface reactions is strongly dependent on surface structures [1–3]. Study of reaction dynamics and its correlation to substrate structures are key issues to fully understand surface reactions at an atomic level. Such an understanding will provide clues for developing superior catalysts, electrodes and material growth processes. Information on structures of transition states (TSs) and microscopic pictures of dynamical events at the moment of bond rupture and bond formation can be obtained by measurements of translational [2, 3], rotational and vibrational [4–7] energies. Determination of TS structures on various surfaces is indispensable for elucidating the origin of the above surface-dependent activities. In order to obtain structural information, such measurements should be performed in angle-resolved (AR) forms.

AR detection of desorbing products in surface reactions and on surface scattering processes has been extensively conducted and has provided information on the dynamics [8–14]. However, information on dynamics in surface reactions has been limited compared with that on dynamics in gas-phase reactions, mainly for two reasons. First, the energies of products easily flow into substrates [15], and thus energies of nascent products at the moment of product formation cannot be easily determined. Second, AR measurements of the internal energies of products have long been lacking.

In gas-phase reactions, detailed shapes of the potential energy surface have been determined through measurements of internal energies in AR forms [16]. On the other hand, in surface reactions, there have been very few works in which AR measurements of internal (only rotational) energy in photo- and electron-induced desorption were carried out [17–19] (yet no significant angular dependence was found). In the last 25 years, non-AR measurements of internal energies of product CO₂ in thermal CO oxidation have been conducted by means of infrared-emission [20–51] (chemiluminescence) and infrared absorption [52, 53].

AR measurements of chemiluminescence of product CO₂ have recently become possible [54–58]. In this review, the method and results of measurements of internal energies of AR product CO₂ in thermal CO oxidation on Pd surfaces are described, and a new approach to TS structures and microscopic pictures of energy partition dynamics is presented.

II. INFORMATION OBTAINED FROM ENERGIES OF PRODUCTS

In many reactions, it is difficult to study dynamical processes and TS structures at moment of the bond formation and bond breaking. In the case of photo-induced reaction, ultrashort light pulses are used to observe time-resolved processes of chemical reactions [59]. In the case of thermal reaction, dynamical and structural information at the moment of reactions can be obtained through measurements of translational, rotational and vibrational energies of products.

CO oxidation proceeds through (1) adsorption of CO and dissociative adsorption of O₂, (2) diffusion of CO towards an O adatom to form a TS (O-CO-metal complex), and (3) repulsive desorption of CO₂, as shown in Fig. 1. Since the bond between product CO₂ and the surface is weak, CO₂ is immediately emitted into the gas-phase. Thus, CO₂ has memory of structures and dynamical events during processes (2) and (3). This memory is maintained in translational, vibrational and rotational energies of CO₂ which are excited during processes (2)-(3) depending on the structure of TS and shapes of potential energy surfaces. By analyzing these energies, it is possible to estimate the structure and dynamics during processes (2)-(3).

In CO oxidation, CO approaches O to form a TS since diffusion of CO is much faster than that of O [2, 59]. The TS has Pd-O, Pd-C, and new O-C bonds [61–66]. When CO₂ forms, it receives strong repulsion from the substrate. This is Pauli repulsion [6], which is operative between electrons of CO₂ and those of the Pd substrate when Pd-O and Pd-C bonds become antibonding. In many desorption processes, the product receives repul-
tion along the direction of the bond that breaks. In many CO$_2$ formation processes, CO$_2$ is desorbed in the direction normal to the CO$_2$ formation site [2]. The sum of repulsions along Pd-O and Pd-C bonds may result in a repulsion of which the direction is close to normal to the formation site, although the direction of each bond may not be normal to the formation site. The translational temperature ($T_{\text{trans}}$) of CO$_2$ is highly excited compared with the surface temperature ($T_{\text{surf}}$), showing a maximum at the collimation angle [2]. Thus, on surfaces that consist of two facets with different inclination angles, dynamics can be separately studied for each CO$_2$ formation site from angular dependence of flux and $T_{\text{trans}}$.

Vibrational energy of CO$_2$ is excited depending on degrees of bending, shrinking and stretching of the TS compared with gas-phase CO$_2$. On the other hand, rotational energy of CO$_2$ is excited if the TS receives a repulsion from a surface at a position far from the center-of-mass of CO$_2$. Results of non-AR measurements of infrared emission and absorption showed that rotational and vibrational energies of product CO$_2$ were also highly excited [20–53]. Kunimori’s group showed that both rotational and vibrational energies are dependent on surface structures. Structural information should be more clearly obtained through AR measurements of internal energies, but such measurements have long been lacking due to extremely weak signals that are lower by three orders compared with those in non-AR measurements. The results of the present AR measurements of internal energies provide new insights into CO$_2$ formation processes as described below.

It is difficult to evaluate whether the energies of CO$_2$ reflect a TS structure ((2) in Fig. 1(b)) or the shape of the potential energy surface ((2)-(3) in Fig. 1(b)) at the moment of final breaking of a product-substrate bond after formation of the product. In the case of N$_2$O+CO reaction on Rh(110), the translational energy of product N$_2$ reflects N$_2$-substrate interaction after N$_2$ product formation [67]. On the other hand, CO$_2$ desorption in CO oxidation on metal surfaces seems to be a simple and smooth process [64]. Thus, in this review it is assumed that energies of CO$_2$ directly reflect TS structures.

### III. EXPERIMENTAL METHOD AND APPARATUS

In many studies, internal energies of desorbing molecules have been analyzed by using resonance enhanced multiple photon ionization (REMPI) and laser-induced fluorescence techniques [4–7], the sensitivities of which are very high, thus enabling measurements even under ultra-high vacuum conditions. However, in the case of CO$_2$, only measurements of infrared emission and infrared absorption, of which sensitivities are extremely weak, are applicable to study internal energies [20–53].

In the present works, infrared emission from product CO$_2$ was detected. Since product CO$_2$ is vibrationally excited, infrared lights are emitted through relaxation of the vibration of CO$_2$ (chemiluminescence). CO$_2$ has three vibrational modes, symmetric stretch (S), bending (B), and antisymmetric stretch (A) modes, as shown in Fig. 2. In the present study, chemiluminescence due to relaxation of A mode ($n_s, n_b, n_a \rightarrow n_s, n_b, n_a - 1$) from CO$_2$ after passing through two slits for angle selection was detected [54], $n_s$, $n_b$, and $n_a$ being the quantum numbers of S, B and A modes, respectively.

There are two major difficulties in measurements of chemiluminescence from AR-CO$_2$. One difficulty is that chemiluminescence only from product CO$_2$ before being scattered by other molecules is detected in AR measure-
FIG. 3: Outline of angle-resolved emission apparatus. It consists of three chambers separately pumped by individual turbo-molecular pumps, that is, a reaction chamber, a collimator housing, and an emission collector chamber. FT-IR in a separate vacuum chamber is connected to the emission collector chamber through a CaF$_2$ window. Dewars with a cooling reagent are connected separately to the optical lens, mirror and copper shields, and copper cylinder.

ments since the direction of CO$_2$ changes in random directions after scattering. Collision between CO$_2$ and reactant molecules should therefore be minimized, and scattered CO$_2$ should be eliminated by strong pumping. The other difficulty is that the intensities of weak chemiluminescence in AR measurements become lower by three orders compared to those in non-AR measurements. To detect chemiluminescence, the background emissions from the apparatus should be eliminated and spectra should be accumulated for a long period (typically one week for a single spectrum at a fixed desorption angle).

A schematic illustration of the apparatus is given in Fig. 3 [54]. It consists of three parts, a reaction chamber of a cylindrical shape, a collimation chamber that has two slits, and an emission collector chamber. These chambers are separately pumped by individual turbo-molecular pumps.

In the upper part of the reaction chamber, a palladium crystal of 10 mm in diameter is cleaned by Ar$^+$ sputtering and annealing in an oxygen atmosphere. Then the crystal is transferred to the center of the reaction chamber. To proceed to the CO oxidation, the sample crystal is kept at a desired $T_{\text{surf}}$, by resistive heating. The reactants O$_2$ and CO are sprayed through four gas dosers. In order to change the desorption angle, the sample crystal and dosers are rotated together without changing the geometric conditions of the reactant exposure. The emitted product CO$_2$ passes through the two slits and enters the emission collection chamber. In the emission collection chamber, chemiluminescence from product CO$_2$ is collected by a CaF$_2$ lens and a tilted gold-coated spherical mirror and transferred to a CaF$_2$ window and then to an FT-IR spectrometer outside the chamber. A quadrupole mass spectrometer is also attached in the emission collector chamber to measure the CO$_2$ yield in the AR form.

A sample of 10 mm in diameter is set as close as possible (3 to 4 mm) from the first slit (Fig. 4). About 75% of the product CO$_2$ passes through the first slit before scattering at a reactant pressure of $3.8 \times 10^{-3}$ Torr in the reaction chamber. No collision actually takes place after the first slit because the pressures of the collimation and emission collector chambers are kept below $1 \times 10^{-5}$ Torr and $1 \times 10^{-7}$ Torr, respectively. Since only a small fraction of the scattered CO$_2$ can pass through the second slit, the surviving AR-CO$_2$ without being scattered reaches more than 99% of the total CO$_2$ flowing out of the second slit into the collector chamber. The resultant signal intensity is reduced to about 0.1% of that in non-AR measurements. This is primarily due to the change in the setting of the emission collector and the reduction in reactant pressures. The signal is so weak that background infrared emission must be minimized by cooling a graphite-coated copper shield surrounding the collection area, including the optics. Thus, data collection takes about one week for a single emission spectrum. To accurately analyze these very weak chemiluminescence spectra, the signal intensities were treated as complex numbers, and the contribution from background emission from the FT-IR spectrometer itself with an unknown phase was accurately eliminated [68].
IV. ANALYSIS OF CHEMILUMINESCENCE SPECTRA

A. Outline of analysis

In high resolution (0.012 cm$^{-1}$) measurements of chemiluminescence in which the population of each of the initial rovibrational states can be separately obtained, it takes 12 hours to obtain a single spectrum even in non-AR measurements at a reaction pressure as high as 10$^{-2}$ Torr for CO oxidation on polycrystalline surfaces [25, 26]. On single crystal surfaces, the rates of CO oxidation are smaller and therefore measurements are conducted in non-state-resolved forms with a low resolution (4 to 8 cm$^{-1}$) as was done by Kunimori’s group [30, 33, 34, 36-51]. Thus, in the present AR measurements on single crystal surfaces, a low resolution of 4 cm$^{-1}$ was chosen.

It is well known that the populations of rotational and the three vibrational modes (S, B and A modes) are expressed well by rotational and three vibrational temperatures, $T_{rot}$, $T_S$, $T_B$, and $T_A$ [20-42, 42, 44-53]. Low-resolution chemiluminescence spectra due to the decay of A mode show a broad peak in the range from 2200 to 2400 cm$^{-1}$. The basic principle for analysis of low-resolution chemiluminescence spectra was developed by Haller’s group [24] and Kunimori’s group [46], and was applied in the present works after improvements in accuracy. Since chemiluminescence occurs through relaxation of A mode, temperature of A mode ($T_A$) can be determined from chemiluminescence intensity. Then other temperatures are determined by comparison of the width and position of experimental and simulated spectra. The spectrum is more red-shifted due to the unharmonic nature of vibration when each vibrational temperature for S, B and A modes ($T_S$, $T_B$ and $T_A$) increases. Therefore, the vibrational temperatures averaged over S and B modes ($T_{sb} = T_B = T_S$) can be estimated from the position of the center of spectra when $T_A$ is known. Each vibrational temperature of S and B mode cannot be separately determined only from the degree of red shift. On the other hand, the spectrum is wider when rotational temperature ($T_{rot}$) is high. Thus, $T_{rot}$ can be obtained from the width of spectra.

B. Analysis of Chemiluminescence Intensity to Determine $T_A$

The intensity of chemiluminescence from AR product CO$_2$ was analyzed in comparison with that from high-temperature reference CO$_2$ with known $T_A$ produced by a molecular beam source, and $T_A$ of product CO$_2$ was determined [57, 58]. Either a Pd(111) surface or diffusive beam source (1400 K) of reference CO$_2$ was used by Kunimori’s group [57, 58]. After the second slit, the chemiluminescence from product CO$_2$ and reference CO$_2$ after passing through the two slits was detected in the emission corrector chamber. The chemiluminescence intensities were normalized by the mass signals of CO$_2$ measured by a quadrupole mass spectrometer set after the second slit. The reference CO$_2$ was made to have angular distribution and temperature similar to those of product CO$_2$ on Pd(111) so that all conditions of chemiluminescence measurements are invariant for product and reference CO$_2$.

The construction of the beam source is shown in Fig. 5a. The chemiluminescence from this CO$_2$ beam was gathered in the same way as that for the product CO$_2$ in CO oxidation. CO$_2$ was introduced into a Mo tube heated to 1400 K by a heater made of a Ta wire. The temperature at the center of the Mo tube was monitored with a thermo-couple. This tube was surrounded by Ta double shields and copper double shields cooled by water, and the surface of the outermost copper shield was kept below 470 K. The diameter of the outermost shield is 27 mm and thus this beam source could be set in front of the first slit (Fig. 5(b)), the distance between the slit and the opposite side of the reaction chamber being only 33 mm. At the upper entrance to the Mo tube, the flow of CO$_2$ was interrupted by a Mo plate and then CO$_2$ penetrated through a capillary hole of 0.5 mm in diameter and 4 mm in length. Then the flow of CO$_2$ was laterally directed through the final nozzle. This nozzle is a Mo plate of 1 mm in thickness and 10 mm in diameter with seven holes that are each 1 mm in diameter. Each hole, of which the length and diameter are equal, yields an angular distribution of CO$_2$ close to a cos$^6$θ form [69]. Thus, the resultant distribution of reference CO$_2$ is close to that of product CO$_2$ in CO oxidation on a Pd(111) crystal of 10 mm in diameter. The position of the beam source was adjusted by checking images of the beam source reflected by two mirrors set below the beam source in the reaction chamber (view 1) and after two slits in the emission collector chamber (view 2).

Each chemiluminescence spectrum (resolution of 4 cm$^{-1}$) from product CO$_2$ (Fig. 6(a)) and reference (Fig. 6(c)) CO$_2$ shows a broad peak consisting of the contributions of initial rovibrational states corresponding to a large number of initial rovibrational states. First, the values of $T_{rot}$ and vibrational temperature $T_{vib}$ that is averaged over $T_S$, $T_B$ and $T_A$ of the reference CO$_2$ were determined by curve-fitting of the experimentally obtained spectrum with simulated ones since $T_S$, $T_B$ and $T_A$ cannot be separately obtained only from the red shift of spectra. The method of simulation is described in the next section. In the simulation, the ratio of red shift with increases in $T_S$, $T_B$, and $T_A$ was about 1:2:1.3. $T_{vib}$ can be obtained as an optimum value assuming $T_{vib} = T_A = T_B = T_S$ in the simulation. The experimental spectrum lies at a lower (higher) wavelength than the simulation for $T_{vib} = 1100$ (1300) K (Fig. 6(d)), showing the error bar close to 100 K. The thick curve in Fig. 6(c) shows the optimum simulated result yielding $T_{vib} = 1200$ K and $T_{rot} = 1150$ K. Since these values of $T_{vib}$ and $T_{rot}$ are close to each other, the internal modes are almost in equilibrium, i.e., $T_A \approx 1200$ K. The total chemiluminescence intensity changes with $T_A$ in the following form as shown by the solid curve in Fig. 6(e):

$$I_{total} = \sum_{n=1}^{\infty} R_n^2 \exp(-E_{na}/kT_a) - \sum_{n=0}^{\infty} \exp(-E_{na}/kT_a),$$

where $R_n^2$ is Frank-Condon factor, and $E_{na}$ is the energy of antisymmetric vibration. Thus, $T_A$ of product CO$_2$ was obtained by comparing total intensities of the chemiluminescence normalized to the CO$_2$ mass signals from product CO$_2$ and that from reference CO$_2$ in Fig. 6(e).
FIG. 5: The structure and setup of the high-temperature molecular beam source.

Fig. 6(e), the theoretical curve is normalized so that \( I_{\text{total}} \) at \( T_a = 1200 \text{ K} \) (\( T_a \) of reference CO\(_2\)) becomes unity. The obtained values for \( T_a \) are 1300 K.

C. Analysis of Band Center and Width of Chemiluminescence Spectra to Determine \( T_{\text{sb}} \) and \( T_{\text{rot}} \)

\( T_{\text{rot}} \) and \( T_{\text{sb}} \) can be analyzed by comparison with experimental and simulated spectra [24, 46]. In the program of simulation, \( T_{\text{rot}}, T_s, T_b, \) and \( T_a \) (already determined in the above section) can be separately input as four parameters. However, the temperature averaged over S and B modes (\( T_{\text{sb}} \)) and \( T_{\text{rot}} \) of product CO\(_2\) was determined assuming \( T_{\text{sb}} = T_s = T_b \) since \( T_s \) and \( T_b \) could not be separately estimated only from the degree of red shift. The contribution of B mode to \( T_{\text{sb}} \) is twice that of S mode since CO\(_2\) has two kinds of B modes of which vibrational directions are perpendicular to each other.

In the simulation, the line positions presented in the Hitran database were used [70]. In addition, these line positions were linearly extended for transitions from higher rovibrational states. In the simulation, 1,487 vibrational bands, each of which contains transitions from initial rotational states from \( J = 0 \) to \( J = 270 \), were used. In this case, simulated spectra cover about 98% and 95% of the total emission intensities at \( T_{\text{vib}} = 2000 \text{ K} \) and \( T_{\text{vib}} = 2500 \text{ K} \), respectively. The other transitions omitted in the simulation should yield smooth tails below 2200 cm\(^{-1}\) outside the main peak. Neglecting these tails should hardly affect the estimation of \( T_{\text{rot}} \) and \( T_{\text{sb}} \). The intensity of each chemiluminescence line is expressed by

\[
I = \exp \left( -E_{n_1n_2}/kT_{\text{sb}} \right) \times \exp \left( -E_{n_2}/kT_{\text{rot}} \right) R^2L/Z_vZ_{\text{rot}},
\]

where \( E_{n_1n_2}, E_{n_3}, \) and \( E_{\text{rot}} \) are the sum of energies of S and B modes, energy of A mode, and rotational energy of the initial rovibrational state, respectively. It was assumed that \( E_{n_3} \) of the molecules with vibrational quantum numbers \((n_1, n_2, n_3)\) is equal to the antisymmetric vibrational energy of the molecule in \((0, 0, n_3)\) given by the database. \( E_{n_1n_2} \) of the molecules with vibrational quantum numbers \((n_1, n_2, n_3)\) was assumed to be \( E_{n_1n_2n_3} - E_{n_3} \), where \( E_{n_1n_2n_3} \) is the total vibrational en-
ergy given by the database. \( Z_v \) and \( Z_{\text{rot}} \) are partition functions corresponding to all vibrational and rotational modes, respectively. Frank-Condon factor, \( R_e^2 \), was obtained from the database [69] and linearly extended for all rovibrational states. \( L \) is Honl-London factor and is given by the formulas below.

\[
L_R = \frac{(J'' + 1 + l)(J'' + 1 - l)}{J'' + 1} \quad (R\text{-branch}) \quad (2)
\]

\[
L_P = \frac{(J'' + l)(J'' - l)}{J''} \quad (P\text{-branch}), \quad (3)
\]

where \( J'' \) is the rotational quantum number in the final state, and \( l \) is angular momentum associated with the bending mode. Due to the selection rule involving the nuclear spin, only even numbers and odd numbers are taken into account for \( J'' \) values in the \( R\)-branch and \( P\)-branch, respectively. The thick curve in Fig. 6(a) shows the optimum result yielding \( T_a = 1300 \) K (obtained by Fig. 6(e)), \( T_{\text{th}} = 2450 \) K, and \( T_{\text{rot}} = 350 \) K.

V. RESULTS

A. Pd(111)

Generally, \( \text{CO}_2 \) formation rate changes with changes in temperature and ratio of exposure of \( \text{O}_2 \) to that of CO (\( \text{O}_2/\text{CO} \)) [1, 2]. Figure 7 shows the rate of \( \text{CO}_2 \) formation versus the surface temperature (\( T_{\text{surf}} \)) on Pd(111) for various \( \text{O}_2/\text{CO} \) exposure ratios at a fixed total exposure (the sum of exposure of \( \text{O}_2 \) and that of CO) of \( 4.5 \times 10^{17} \) molecules/cm²s. At each ratio, with increasing \( T_{\text{surf}} \), the \( \text{CO}_2 \) formation becomes noticeable above 500 K and shows a maximum at around 650-700 K (\( T_{\text{max}} \)). Below \( T_{\text{max}} \), the oxygen dissociation is rate-determining in the CO oxidation, and the surface is highly covered by CO, i.e., CO(a) \( \approx \) O(a) (inhibited region). The \( \text{O}_2 \) dissociation increases at higher \( T_{\text{surf}} \) by increasing vacant sites through enhanced CO desorption. On the other hand, above \( T_{\text{max}} \), the coverage of CO becomes small, resulting in decreasing \( \text{CO}_2 \) formation (active region). \( T_{\text{max}} \) shifts to higher values as the \( \text{O}_2/\text{CO} \) ratio decreases because of the higher temperature required to yield vacant sites at high CO pressures [1, 2]. The following AR measurements were performed for the optimum CO oxidation at \( T_{\text{surf}} = 700 \) K and \( \text{O}_2/\text{CO} = 1/2 \).

The measurements were limited to the plane along the [112] direction since the azimuth effect is negligibly small on a (111) surface [2]. \( \text{CO}_2 \) desorption was sharply collimated along the surface normal in a \( \cos^6 \theta \) form, where \( \theta \) is the desorption angle (polar angle), as shown in Fig. 8. This indicates the repulsive desorption of CO along the surface normal, i.e., nascent \( \text{CO}_2 \) appears on a repulsive part of potential energy surface (see Fig. 1(b)). The values of \( T_a \), \( T_{\text{th}} \), and \( T_{\text{rot}} \) are summarized as functions of desorption angle in Fig. 9 [55, 57]. \( T_{\text{th}} \) decreases as \( T_a \) and \( T_{\text{rot}} \) increase as the desorption angle increases. These results indicate that rotational, A and B modes differently couple to the translational mode in their excitation processes. When the TS leaves the surface to become \( \text{CO}_2 \), the excess energy is partitioned into translational, vibrational and rotational modes. The bent TS [61–64] becomes linear and the C-O bond lengths approach that of gas-phase \( \text{CO}_2 \), resulting in vibrational motions. These structural changes from TS to linear \( \text{CO}_2 \) may induce an impulse accelerating the translational motion in the same direction as that of vibration; i.e., vibrational and translational motions in the same direction are thought to strongly couple to each other. If the TS is parallel to the surface, the directions of vibrational motions of A and B modes are parallel and perpendicular to the surface, respectively (Figs. 10(a) and 10(b)), and thus desorption of \( \text{CO}_2 \) with highly excited A and B modes is promoted in parallel (inclined) and perpendicular directions, respectively.

Considering the results of ab initio calculation of a TS structure, a more detailed picture could be obtained as follows. The TS is nearly surface-parallel and bent [62–64] as illustrated in Fig. 10(c) leading to the final state in which the \( \text{CO}_2 \) molecule is lying horizontally. In the TS, three bonds of Pd-O, Pd-CO, and O-CO compete with
desorption of CO to the center-of-mass, resulting in the normally directed repulsion in the antisymmetric (surface normal) direction at the C end close to the surface normal direction. Nascent CO is linear and more antisymmetric with respect to the C atom. When the Pd-O bond is weak (Fig. 10(d)), the TS may become more bent and more antisymmetric in the y-z plane (Fig. 11(b)). At this O2/CO ratio, the anisotropy was reversed. That is, all of these temperatures decreased with increases in the desorption angle in [110], while these temperatures increased in [001].

The above results show clear dependence of $T_a$, $T_{sb}$, and $T_{rot}$ of product CO2 on polar and azimuthal angles. Since results for Pd(110) at O2/CO = 1/2 and at O2/CO = 2 are quite different, the observed angular dependence of $T_a$, $T_{sb}$, and $T_{rot}$ contains information on structures of surfaces and TS structures on them. At O2/CO = 1/2 (Pd(110)-(111) × 1), $T_a$, $T_{sb}$ and $T_{rot}$ in the y-z plane were constant, while these temperatures decreased with increases in $\theta$ in the x-z plane, as shown in Fig. 11(a). This indicates that CO2 with high rovibrational energy can easily move in the y-z plane but that its motion in the x-z plane is hindered. It is thought that CO approaches an oxygen atom at the bottom of the atomic trough to form a TS on this surface [2, 73]. The present results suggest that the TS is inclined in the y-z plane and that it receives repulsion along the z-axis, leading to rotational motion of CO2 in the y-z plane (Fig. 12). Nascent CO2 can easily move in the y-z plane, while the motion of CO2 in the x-z plane is interrupted by rows of the 1st Pd layers. Previous studies showed that with increases in $\theta$, the translational temperature and desorption flux of CO2 gradually decrease in the y-z plane and decrease rapidly in the x-z plane [2, 72], consistent with restricted motions.

Internal energies of product CO2 in CO oxidation on Pd(111) were previously studied by chemiluminescence measurements in non-AR forms by Kunimori’s group [34, 38, 46, 49]. In those works, both vibrational and rotational temperatures were highly excited, consistent with the present results. They reported that $T_a$ significantly increased when the ratio of O2/CO decreased [46]. Their values of $T_{rot}$ (1130 K at $T_{surf} = 650$ K and 400 K at $T_{surf} = 850$ K) [34, 38] are higher than those of the present results. This may be partly because the methods of simulation, especially the number of vibrational bands taken into account in simulation programs, are different.

B. Pd(110)

A Pd(110) surface consists of ditch of atomic rows aligned in the [110] direction. Therefore, energies are expected to change depending on azimuthal directions. Measurements are conducted at O2/CO=1/2 and O2/CO=2 at $T_{surf} = 600$ K [55, 58]. It is known that the (1×1) structure of clean Pd(110) (Fig. 11) is reconstructed into a missing-row structure (i.e., c(2×4)-O) above 360 K when the oxygen coverage is high [71, 72]. Therefore, the surface structures at $T_{surf} = 600$ K are thought to be (1×1) and missing-row structures at O2/CO=1/2 and O2/CO=2, respectively.

Figure 11(a) shows angular dependence of $T_a$, $T_{sb}$, and $T_{rot}$ in [110] and [001] directions at O2/CO = 1/2. $T_a$, $T_{sb}$ and $T_{rot}$ at $0^\circ$ are 1400 K, 1550 K and 950 K, respectively. All temperatures remained constant when the desorption angle changed in [110], while these temperatures decreased in [001]. When O2/CO increased to 2, $T_a$ significantly decreased to 1000 K at $0^\circ$. $T_{rot}$ also decreased to 800 K at $0^\circ$, as shown in Fig. 11(b). At this O2/CO ratio, the anisotropy was reversed. That is, all of these temperatures decreased with increases in the desorption angle in [110], while these temperatures increased in [001].

The above results show clear dependence of $T_a$, $T_{sb}$, and $T_{rot}$ of product CO2 on polar and azimuthal angles. Since results for Pd(110) at O2/CO = 1/2 and at O2/CO = 2 are quite different, the observed angular dependence of $T_a$, $T_{sb}$, and $T_{rot}$ contains information on structures of surfaces and TS structures on them. At O2/CO = 1/2 (Pd(110)-(1×1)), $T_a$, $T_{sb}$ and $T_{rot}$ in the y-z plane were constant, while these temperatures decreased with increases in $\theta$ in the x-z plane, as shown in Fig. 11(a). This indicates that CO2 with high rovibrational energy can easily move in the y-z plane but that its motion in the x-z plane is hindered. It is thought that CO approaches an oxygen atom at the bottom of the atomic trough to form a TS on this surface [2, 73]. The present results suggest that the TS is inclined in the y-z plane and that it receives repulsion along the z-axis, leading to rotational motion of CO2 in the y-z plane (Fig. 12). Nascent CO2 can easily move in the y-z plane, while the motion of CO2 in the x-z plane is interrupted by rows of the 1st Pd layers. Previous studies showed that with increases in $\theta$, the translational temperature and desorption flux of CO2 gradually decrease in the y-z plane and decrease rapidly in the x-z plane [2, 72], consistent with restricted motions.

Each other. When the Pd-CO bond is strong and the Pd-O bond is weak, the TS may become more bent and more antisymmetric with respect to the C atom and the surface normal direction. Nascent CO2 receives repulsion in the symmetric (surface normal) direction at the C end close to the center-of-mass, resulting in the normally directed desorption of CO2 with high $T_{sb}$, low $T_a$ and low $T_{rot}$. In contrast, when the Pd-O bond is strong and the Pd-CO bond is weak (Fig. 10(d)), the TS may become more linear and more antisymmetric with respect to the C atom and the surface normal direction. Nascent CO2 receives repulsion in the antisymmetric (inclined) direction at the O end far from the center-of-mass, resulting in inclined desorption of CO2 with high $T_a$, high $T_{rot}$, and low $T_{sb}$.
FIG. 11: Angular dependence of $T_a$ (squares), $T_{sb}$ (triangles) and $T_{rot}$ (circles) on Pd(110). Opened and closed symbols are results in $[1\bar{1}0]$ and $[001]$ directions, respectively. (a) and (c) show results at O$_2$/CO = 2 and 1/2, respectively.

On the other hand, on Pd(110) with missing rows, $T_a$, $T_{sb}$ and $T_{rot}$ increased with increases in $\theta$ in the $x$-$z$ plane and decreased in the $y$-$z$ plane, indicating that desorption of CO$_2$ with high rovibrational energy is promoted at large $\theta$ in the $x$-$z$ plane. On this surface, oxygen atoms form zigzag chains along the $y$-axis near protruding rows of the 1st Pd layer (Fig. 13(a)) [71] and the oxygen at the end of the chain is highly reactive with CO [74]. Thus, CO oxidation should occur near the 1st Pd layer. The TS on the protruded Pd row can be oriented in the $x$-$z$ plane and rotational motion of TS (or nascent CO$_2$) in the $x$-$z$ plane is easy as shown in Fig. 13(a). Depending on the position and inclination of the TS, the direction of repulsion from protruding rows may shift from the surface normal in the $x$-$z$ plane, and the torque operative to the TS may also change. This effect leads to desorption of CO$_2$ with high rotational energy at large $\theta$ in the $x$-$z$ plane. For CO oxidation on Pt(110) with missingrows, which is similar to the present Pd(110) with missingrows, a TS inclined in the plane perpendicular to the atomic rows was predicted by ab initio calculations [75], consistent with the prediction in the present work.

In the following, more detailed consideration of TS structures is presented. As already mentioned, in the TS, bonds of Pd-O, Pd-CO, and O-CO compete with each other [61–63]. When the Pd-O bond is strong and the Pd-CO bond is weak (TS(\alpha) in Fig. 13(b)), the distance between O and Pd is short and that between C and Pd is long. During desorption, nascent CO$_2$ receives repulsion at the O end far from the center-of-mass. This nascent CO$_2$ appears on the inclined (111) facet, and therefore the direction of repulsion is inclined toward the (111) facet normal, leading to desorption of CO$_2$ with high $T_{rot}$ in inclined directions.

In another case, CO may bond with Pd atoms in the 1st layer to form a TS and O may be somewhat repelled by CO (TS(\beta) in Fig. 13(c)) since theoretical modeling of CO oxidation often shows that the competition between CO and O to bind the same Pd atom leads to breaking of the O-Pd bond and repelling of O by CO to an adjacent site [61–63]. In this case, nascent CO$_2$ receives repulsion at the C end close to the center-of-mass, leading to desorption of CO$_2$ with low $T_{rot}$. Since CO$_2$ appears near a protruding row of Pd atoms, the repulsion is directed in the surface normal. Thus, $T_{rot}$ is low at the surface normal. A TS that is similar to TS(\beta) may be formed near the protruding row of Pd atoms also when CO approaches O at the opposite side of the zigzag chain (TS(\gamma) in Fig. 13(d)). This TS would show desorption dynamics similar to that of TS(\beta). In both cases, the geometry of TS can be more linear and closer to that of gas-phase CO$_2$ since the substrate structure at the protruded atomic row is widely opened. Thus, the bending and shrinking/stretching of the TS or nascent CO$_2$ forced by the substrate structure should be less, resulting in lower $T_a$ and $T_{sb}$ at the surface normal direction.

For the TS geometries proposed above, motions of symmetric stretch, bending, and antisymmetric stretch modes are in the $y$-$z$ plane on Pd(110)(1×1) and in the $x$-$z$ plane on Pd(110) with missingrows. The present results indicate that desorption of CO$_2$ with high vibrational energy is concentrated in the $y$-$z$ plane on Pd(110)(1×1) (Fig. 11(a)) and in the $x$-$z$ plane on Pd(110) with missingrows (Fig. 11(b)). This is consistent with the model of vibration-translation coupling proposed for Pd(111) in section V.A that vibrational and translational motions with the same direction strongly couple to each other.
Since motions of the antisymmetric mode and bending mode are perpendicular to each other in a single CO$_2$ molecule, it is expected that $T_a$ and $T_{sb}$ are enhanced at different desorption angles. Nevertheless, such a difference was not observed on these Pd(110) surfaces. This is probably because the TS is inclined at various angles in the y-z plane on Pd(110)(1×1) and in the x-z plane on Pd(110) with missing rows.

In the present study, it was found that $T_a$ is strongly dependent on O$_2$/CO. At O$_2$/CO = 2, $T_a$ is about 1000 K and it increased to about 1400 K at O$_2$/CO = 1/2 and 1500 K at O$_2$/CO = 1/8, while $T_{sb}$ slightly decreased. Such increase in $T_a$ and decrease in $T_{sb}$ were previously reported by Kunimori’s group [46]. The values of $T_a$ in the present study are lower than their results (T$_a$ = 1500 K (O$_2$/CO=2) and 2800 K (O$_2$/CO=1/8)), partly because the formula used to estimate $T_a$ (Eq. (1)) is different from that used in the previous study [46]. The increment of $T_a$ in the present study was significant when O$_2$/CO decreased from 2 to 1/2 but less significant when O$_2$/CO decreased from 1/2 to 1/8. When O$_2$/CO decreased from 2 to 1/2, the anisotropy in angular dependence of $T_a$, $T_{sb}$ and $T_{rot}$ was reversed due to surface reconstruction from missing-row to 1×1 structures and change in orientation of TSs from the x-z plane to y-z plane. The increase in $T_a$ is related to this change in TS structure. In the previous work [46], it was proposed that increased $T_a$ is due to the TS structure in which the distance between O and CO is compressed due to increased CO coverage. This mechanism is not inconsistent with the present results.

C. Pd Polycrystalline

Although the structures of polycrystalline have not been elucidated, studies on polycrystalline are important since its structures are thought to be close to those of real catalysts compared with that of single crystal surfaces.

Figure 14 summarizes the angular dependence of $T_{rot}$ and $T_{vib}$ at O$_2$/CO = 1/2 (closed squares and circles) and at O$_2$/CO = 2 (open squares and circles) as a function of the desorption angle [56]. In this preliminary work, $T_a$ and $T_{sb}$ were not separately determined. Both $T_{vib}$ and $T_{rot}$ increase as the desorption angle increases. It can also be seen that $T_{vib}$ and $T_{rot}$ at O$_2$/CO = 2 are higher than those at O$_2$/CO = 1/2. Chemiluminescence intensities normalized by the amount of CO$_2$ increased with increases in desorption angle, indicating increased temperatures of the antisymmetric mode.

On a polycrystalline surface, $T_{vib}$ and $T_{rot}$ have been expected to be independent of the desorption angle due to disordered orientation of grains. Nevertheless, the present work showed remarkable increases in $T_{vib}$ and $T_{rot}$ with increase in the desorption angle, which are quite different from those on Pd(111). This indicates the importance of AR measurements for a full understanding of energy
partition in surface reactions. The enhanced \( T_{\text{vib}} \) at large desorption angles is probably due to contribution from CO\(_2\) formed on inclined formation sites. On Pd polycrystalline, CO\(_2\) molecules should be formed on several kinds of different sites with different inclinations, and desorbing CO\(_2\) is collimated in the direction normal to each formation site. This implies that it is possible to study internal energies of CO\(_2\) formed on each site with different inclinations on stepped or reconstructed single crystal surfaces. For example, \( T_{\text{vib}} \) and \( T_{\text{rot}} \) of CO\(_2\) formed on (111) and (001) facets on Pd(113) or Pt(113) may be separately studied [76, 77].

\[ T_{\text{vib}} \text{ and } T_{\text{rot}} \text{ increase with increases in } O_2/CO \text{ from } 1/2 \text{ to } 2 \text{ as shown in Fig. 14. This is consistent with previous results on a Pd polycrystalline showing that both temperatures increased with increase in oxygen coverage, which was attributed to increased energy of TSs due to repulsion between adsorbates [27].} \]

VI. SUMMARY

Angle-resolved measurements of internal energies have become possible for the first time for thermal surface reactions. Results of measurements of chemiluminescence from AR product CO\(_2\) showed that rotational energy and each of the vibrational energies are strongly dependent on surface structures and on polar and azimuth angles, providing valuable information on structures of transition states and details of energy partition dynamics. The present results emphasize the importance of AR measurements of energies of products for a full understanding of surface reaction dynamics. Together with advanced theoretical works, AR measurements of internal energy will unveil new microscopic features in surface chemical physics.

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