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Mode-dependent coupling between vibration and translation of product CO₂ in CO oxidation on Pd(111)

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The vibrational temperatures of product CO₂ were measured in CO oxidation on Pd(111) as a function of the desorption angle by means of infrared chemiluminescence. The antisymmetric vibration temperature was separately determined from the other vibrational modes from the normalized chemiluminescence intensity. The product CO₂ desorption is sharply collimated along the surface normal. The antisymmetric vibrational temperature increased from 1300 to 1600 K as the desorption angle increased from 0° to 30°, whereas the averaged vibrational temperature over bending and symmetric modes decreased from 2450 to 1530 K. From these angle dependences, an energy partitioning model in repulsive desorption is proposed. © 2008 American Institute of Physics. [DOI: 10.1063/1.2918729]

Elucidation of energy transfer dynamics and structures of transition states (TSs) is an important subject for full understanding of surface reaction.^{1–11} Such an understanding at the atomic level is required to develop superior catalysts, electrodes, and material growth processes. Dynamics and TS structures can be studied by measurements of translational and internal (rotational and vibrational) energies of desorbing products.^{5,12–19} Although angle-resolved (AR) measurements^{5–11} are required to study internal energies to obtain detailed structural information, such measurements have long been lacking in thermal surface reactions because of the difficulty of experiments. In this communication, results of measurements of internal energies of AR product CO₂ in CO oxidation on Pd(111) are presented.

CO oxidation on noble metals is a prototypical surface reaction that has long attracted attention of chemists, physicists, and also mathematicians because of its practical importance and rich phenomena.^{1,5,11–26} Non-AR measurements of internal energies of product CO₂ have been extensively conducted by analysis of chemiluminescence from CO₂^{12–17,19} and infrared (IR) absorption by CO₂.¹⁸ Recently, measurements of internal energies of AR CO₂ have been reported.^{27,28} Although CO₂ has three vibrational modes [symmetry stretch (*S*), bending (*B*), and antisymmetric stretch (*A*) modes], in the above AR study, only rotational temperature (T_{rot}) and vibrational temperature (T_{vib}) averaged over the three modes were determined assuming $T_{\text{vib}} = T_s = T_b = T_a$ (temperatures of *S*, *B*, and *A* modes).

In this communication, mode-resolved AR measurements of vibrational energies of product CO₂ are presented. The intensity of chemiluminescence from AR product CO₂ was analyzed in comparison with that from high-temperature reference CO₂ from a newly developed molecular beam source, and the degree of excitation of *A* mode was separately determined from those of other vibrational modes. It was found that the excitations of *A* and *B* modes differently

correlate with translational directions. In many chemical reactions, it is difficult to experimentally study the moment of reaction, while formation processes of TS structures in surface reactions (including CO oxidation^{20–25}) have been studied in detail by *ab initio* calculations. The results of the present study provide unique information on TS structures and subsequent energy partition dynamics.

The design of the apparatus for analysis of extremely weak IR emission from AR CO₂ has recently been described in detail.²⁷ IR light emitted in relaxation of the antisymmetric stretch mode of CO₂ after passing through two slits for angle selection, $(n_s, n_b, n_a) \rightarrow (n_s, n_b, n_a - 1)$, where n_s , n_b , and n_a are the quantum numbers of *S*, *B*, and *A* modes, respectively, is analyzed by a Fourier transform-IR spectrometer. Either a Pd(111) surface or diffusive beam source (1400 K) of reference CO₂ was set before the first slit, and chemiluminescence from product CO₂ and reference CO₂ was detected. The chemiluminescence intensities were normalized by the amount of CO₂ measured by a quadrupole mass spectrometer after the second slit.

The vibrational temperature of *A* mode was separately determined from the averaged temperature over *B* and *S* modes by a careful calibration of chemiluminescence intensity. To compare the intensity from AR product CO₂ with that from reference high-temperature CO₂, a diffusive molecular beam source was newly developed. The reference CO₂ was made to have similar angular distribution and similar temperature to those of product CO₂ on Pd(111), so that all conditions of chemiluminescence measurements are invariant for product and reference CO₂.

The construction of the beam source is shown in Fig. 1(a). After the CO₂ beam passed the two slits, the chemiluminescence from this CO₂ beam was gathered in the same way as that for the product CO₂ in CO oxidation. CO₂ was introduced into a Mo tube heated to 1400 K by a heater made of a Ta wire. The temperature of the Mo tube was monitored with a thermocouple connected at its middle point. This tube was surrounded by Ta double shields and

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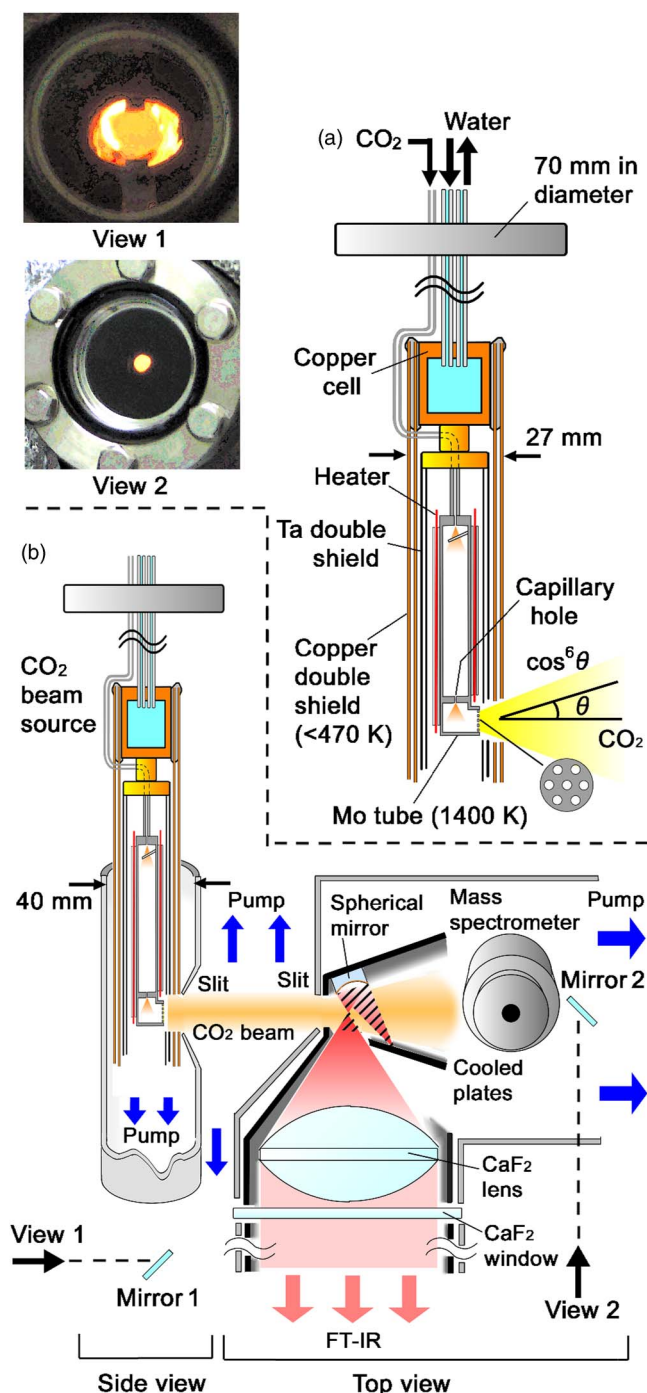


FIG. 1. (Color online) The structure and setup of the molecular beam source.

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. 1(b)], where the distance between the slit and the opposite side of the reaction chamber is only 33 mm. At the upper entrance to the Mo tube, the flow of CO₂ was interrupted by a Mo plate and then CO₂ was emitted through a capillary hole of 0.5 mm in diameter and 4 mm in length. Then, the flow of CO₂ 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. A theoretical

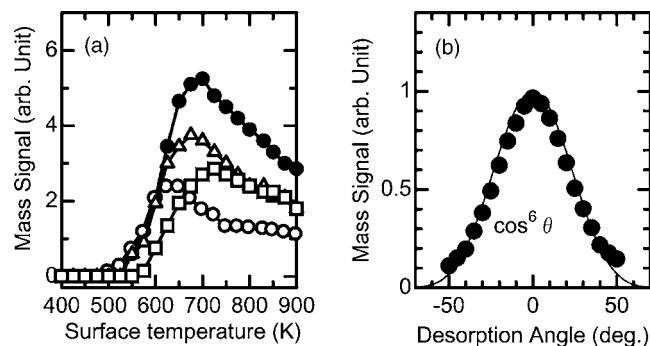


FIG. 2. (a) Rate of CO₂ formation vs T_{surf} . The O₂/CO exposure ratios are 2 (open circles), 1 (open triangles), 1/2 (closed circles), and 1/4 (open squares). The total exposure of CO and O₂ was fixed at 4.5×10^{17} molecules/cm² s, and the O₂/CO ratio was varied as indicated. (b) Angular distribution of product CO₂ in the plane along the $[11\bar{2}]$ azimuthal direction. It is sharply collimated along the surface normal.

calculation showed that each hole of which the length and diameter are equal yields an angular distribution of CO₂ close to a $\cos^6 \theta$ form.²⁹ The resultant distribution is close to that of product CO₂ 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).

Figure 2(a) shows the rate of CO₂ formation versus the surface temperature (T_{surf}) for various O₂/CO exposure ratios at a fixed exposure of 4.5×10^{17} molecules/cm² s. At each ratio, with increasing T_{surf} , the CO₂ formation becomes noticeable at above 500 K and shows a maximum at around 650–700 K (T_{max}). Below T_{max} , the oxygen dissociation is rate determining in the CO oxidation, and the surface is highly covered by CO, i.e., CO(a) $\gg$ O(a). The O₂ dissociation increases at higher T_{surf} by increasing vacant sites through enhanced CO desorption. On the other hand, at above T_{max} , the coverage of CO becomes small, resulting in decreasing CO₂ formation. T_{max} shifts to higher values as the O₂/CO ratio decreases because of the higher temperature required to yield vacant sites at high CO pressures.^{1,5} The following AR measurements were performed for the optimum CO oxidation at $T_{\text{surf}}=700$ K and O₂/CO=1/2.

The measurements were limited only in the plane along the $[11\bar{2}]$ direction, since the azimuth effect is negligibly small on a (111) surface.⁵ Figure 2(b) shows the angular distribution of product CO₂. The CO₂ desorption was sharply collimated along the surface normal in a $\cos^6 \theta$ form, where θ is the desorption angle (polar angle), indicating the repulsive desorption of CO₂ along the surface normal; i.e., nascent CO₂ appears on a repulsive part of potential energy surface.

Each chemiluminescence spectrum (resolution of 4 cm⁻¹) from product CO₂ [Fig. 3(a)] and reference CO₂ [Fig. 3(c)] shows a broad peak consisting of the contributions of transition lines corresponding to a large number of initial rovibrational states. The populations of rovibrational states of product CO₂ are known to be well expressed by the rotational and vibrational temperatures.^{12–19} First, the values

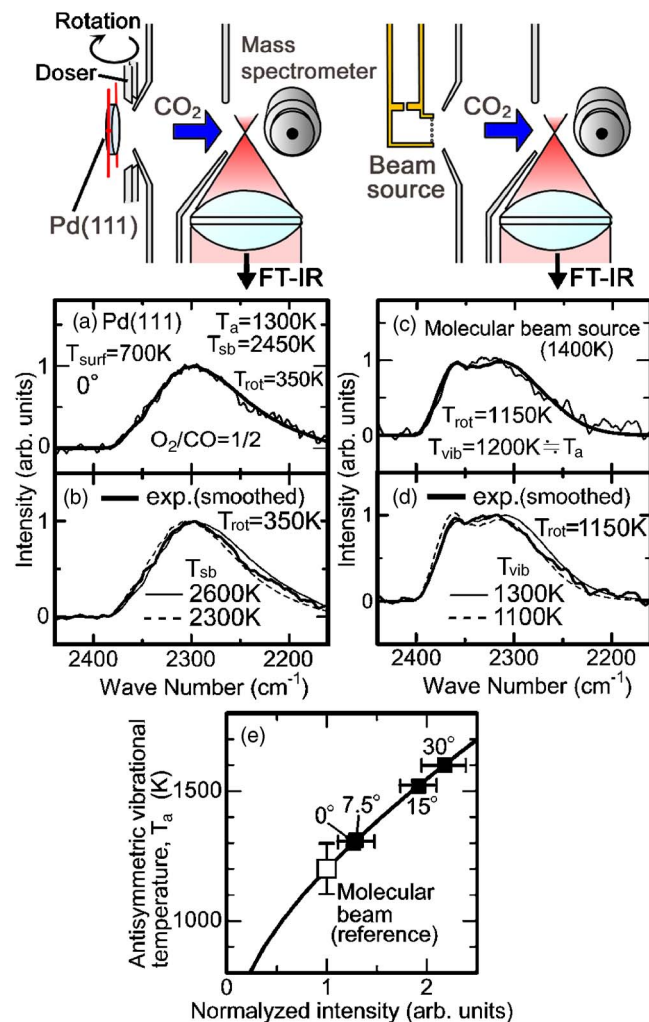


FIG. 3. (Color online) Comparison of chemiluminescence spectra of product CO₂ on Pd(111) at 700 K (The total exposure of O₂ and CO is 4.5×10^{17} molecules/cm²s and the ratio of exposure of O₂ to that of CO (O₂/CO) is 1/2.) and reference CO₂. In (a) (product) and (c) (reference), thin lines and thick curves show experimental and optimum simulated results, respectively. (b) and (d) show smoothed experimental results (thick solid curves) and some simulated curves (thin solid and thin dashed curves), indicating that error bars of T_{sb} and T_{vib} are close to 150 and 100 K. (e) Determination of T_a by plotting chemiluminescence intensity normalized by CO₂ mass signals. The curve indicates theoretical calculation (see text).

of T_{rot} and T_{vib} of the reference CO₂ were determined by curve fitting of the experimentally obtained spectrum with simulated ones.^{12,27,30} The spectrum is wide when T_{rot} is high, while the spectrum is more redshifted when each of T_s , T_b , and T_a is high. In the simulation, the ratio of redshift with increases in T_s , T_b , and T_a was about 1:2:1.3. Since T_s , T_b , and T_a could not be separately estimated only from the degree of redshift, T_{vib} averaged over the three modes (i.e., assuming $T_{vib} = T_a = T_s = T_b$) and T_{rot} were estimated. The experimental spectrum lies at a lower (higher) wavelength than the simulation for $T_{vib} = 1100$ (1300) K [Fig. 3(d)], showing the error bar close to 100 K. The thick curve in Fig. 3(c) shows the optimum simulated result yielding $T_{vib} = 1200$ K and $T_{rot} = 1150$ K. These values are lower than the temperature at the center of the beam source (1400 K), probably because the temperature around the final nozzle is lower. Since these values are close to each other, the internal modes

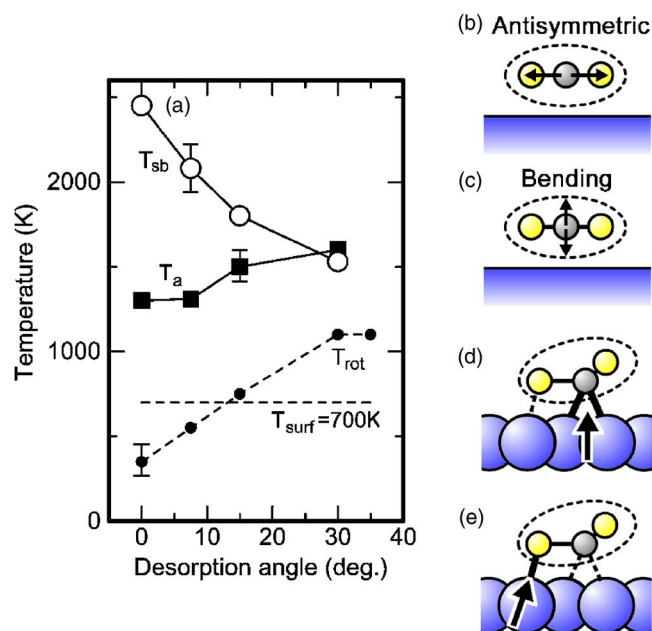


FIG. 4. (Color online) (a) Angular dependence of T_a , T_{sb} , and T_{rot} . The error bars in (a) were estimated without considering the uncertainty of T_a (100 K) of the reference CO₂. An increase in T_a of reference CO₂ by 100 K leads to increases in T_a by about 100 K and decreases in T_{sb} by about 30 K at all desorption angles. (b)–(e) show illustrations of TSs with directions of vibration and repulsion.

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. 3(e):

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

where R_v^2 is Frank–Condon factors and E_{na} is the energy of antisymmetric vibration. Thus, T_a of product CO₂ was obtained by comparing total intensities of the chemiluminescence normalized to the CO₂ mass signals from product CO₂ and that from reference CO₂ in Fig. 3(e). In Fig. 3(e), the theoretical curve is normalized so that I_{tot} at $T_a = 1200$ K (T_a of reference CO₂) becomes unity. The obtained values for T_a are 1300, 1310, 1500, and 1600 K at $\theta = 0^\circ$, 7.5° , 15° , and 30° , respectively. Then, the temperature of the other two vibrational modes (T_{sb}) of product CO₂ was determined by curve fitting assuming $T_{sb} = T_s = T_b$, since T_s and T_b could not be separately estimated only from the degree of redshift. The contribution of the *B* mode to T_{sb} is twice that of the *S* mode, since CO₂ has two kinds of *B* modes of which vibrational directions are perpendicular to each other. The thick curve in Fig. 3(a) shows the optimum result yielding $T_a = 1300$ K [obtained by Fig. 3(e)], $T_{sb} = 2450$ K, and $T_{rot} = 350$ K. A similar estimation of T_a in CO oxidation has previously been reported.²⁹ The values of T_a , T_{sb} , and T_{rot} are summarized as functions of desorption angle in Fig. 4(a). T_{sb} decreases while T_a and T_{rot} increase as the desorption angle increases.

The different angular dependence between T_a and T_{sb} indicates that *A* and *B* modes differently couple to the translational mode in their excitation processes. When TS leaves the surface to become CO₂, the excess energy is partitioned into translational, vibrational, and rotational modes. The bent

TS (Refs. 20–22) becomes linear and the C–O bond lengths approach that of gas-phase CO₂, resulting in vibrational motions. These structural changes from TS to linear CO₂ 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 be strongly coupled to each other. If 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. 4(b) and 4(c)] and, thus, desorption of CO₂ with highly excited *A* and *B* modes is promoted in parallel (inclined) and perpendicular directions, respectively.

A more detailed picture is considered as follows. It is natural to expect that CO approaches O to form an upright TS, since diffusion of CO is much faster than that of O at 700 K. However, theoretical modeling indicates that, even though free diffusion of the O atom does not occur, a TS is formed by motion of both CO (diffusion) and the O atom (movement from threefold to twofold Pd bonding); the transition state has both the C end of CO and the O atom bonded to the same Pd atom. The TS is nearly surface parallel and bent,^{21–23} as illustrated in Fig. 4(d), leading to the final state in which the CO₂ molecule is horizontally lying.

In the TS, three bonds of Pd–O, Pd–CO, and O–CO compete with each other. When the Pd–CO bond is strong and the Pd–O bond is weak, TS may become more bent and more symmetric 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. 4(e)], 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 off center of mass, resulting in inclined desorption of CO₂ with high T_a , high T_{rot} , and low T_{sb} .

In the present work, T_{sb} was higher than T_a , while in the previous work, T_a was higher than T_s and T_b on Pt polycrystalline. Probably to keep Pd–O, Pd–CO, and O–CO bonds, TS must be bent on flat Pd(111) [Fig. 4(d)], resulting in high T_{sb} , while TS can be linear at corrugated step or kink sites on polycrystalline.

The present work showed that the angular dependence of vibrational excitation is mode dependent, which provides

valuable information on TS and dynamics. Together with advanced theoretical works, AR measurements of internal energy will unveil new microscopic features in surface chemical physics.

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