Mode-dependent coupling between vibration and translation of product CO$_2$ in CO oxidation on Pd(111)

Toshiro Yamanaka
Catalysis Research Center, Hokkaido University, Sapporo 001-0021, Japan

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The vibrational temperatures of product CO$_2$ 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 CO$_2$ 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. 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. Non-AR measurements 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 CO$_2$ 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. Non-AR measurements of internal energies of product CO$_2$ have been extensively conducted by analysis of chemiluminescence from CO$_2$ and infrared (IR) absorption by CO$_2$. Recently, measurements of internal energies of AR CO$_2$ have been reported. Although CO$_2$ 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 $T_{vib}=T_s=T_b=T_a$ (temperatures of S, B, and A modes).

In this communication, mode-resolved AR measurements of vibrational energies of product CO$_2$ are presented. The intensity of chemiluminescence from AR product CO$_2$ was analyzed in comparison with that from high-temperature reference CO$_2$ 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) 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 CO$_2$ has recently been described in detail. IR light emitted in relaxation of the antisymmetric stretch mode of CO$_2$ after passing through two slits for angle selection, $(n_s,n_b,n_a)$ → $(n_s,n_b,n_a-1)$, 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 CO$_2$ was set before the first slit, and chemiluminescence from product CO$_2$ and reference CO$_2$ was detected. The chemiluminescence intensities were normalized by the amount of CO$_2$ 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 CO$_2$ with that from reference high-temperature CO$_2$, a diffusive molecular beam source was newly developed. The reference CO$_2$ was made to have similar angular distribution and similar temperature 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. 1(a). After the CO$_2$ beam passed the two slits, 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 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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$^a$Electronic mail: yama@cat.hokudai.ac.jp.
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 calculation showed that each hole of which the length and diameter are equal yields an angular distribution of CO₂ close to a cos⁶ θ form. 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 (Tsurf) for various O₂/CO exposure ratios at a fixed exposure of 4.5x10¹⁷ molecules/cm² s. At each ratio, with increasing Tsurf, the CO₂ formation becomes noticeable at above 500 K and shows a maximum at around 650–700 K (Tmax). Below Tmax, the oxygen dissociation is rate determining in the CO oxidation, and the surface is highly covered by CO, i.e., CO(a) ≈ O(a). The O₂ dissociation increases at higher Tsurf by increasing vacant sites through enhanced CO desorption. On the other hand, at above Tmax, the coverage of CO becomes small, resulting in decreasing CO₂ formation. Tmax shifts to higher values as the O₂/CO ratio decreases because of the higher temperature required to yield vacant sites at high CO pressures. The following AR measurements were performed for the optimum CO oxidation at Tsurf=700 K and O₂/CO=1/2.

The measurements were limited only in the plane along the [112] direction, since the azimuth effect is negligibly small on a (111) surface. Figure 2(b) shows the angular distribution of product CO₂. The CO₂ desorption was sharply collimated along the surface normal in a cos⁶ θ 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. First, the values
of $T_{\text{rot}}$ and $T_{\text{vb}}$ of the reference CO$_2$ were determined by curve fitting of the experimentally obtained spectrum with simulated ones. The spectrum is wide when $T_{\text{rot}}$ 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, $T_{\text{vb}}$ averaged over the three modes (i.e., assuming $T_{\text{vb}}=T_s=T_b$) and $T_{\text{rot}}$ were estimated. The experimental spectrum lies at a lower (higher) wavelength than the simulation for $T_{\text{vb}}=1100$ (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 $T_{\text{vb}}=1200$ K and $T_{\text{rot}}=1150$ 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 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):

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

where $R_n^2$ is Frank–Condon factors and $E_{\text{na}}$ 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. 3(e). In Fig. 3(e), the theoretical curve is normalized so that $I_{\text{tot}}$ at $T_a=1200$ K ($T_a$ of reference CO$_2$) becomes unity. The obtained values for $T_a$ are 1300, 1310, 1500, and 1600 K at $\theta=0^\circ$, 7.5$^\circ$, 15$^\circ$, and 30$^\circ$, respectively. Then, the temperature of the other two vibrational modes ($T_{\text{vb}}$) of product CO$_2$ was determined by curve fitting assuming $T_{\text{vb}}=T_a=T_b$, since $T_a$ and $T_b$ could not be separately estimated only from the degree of redshift. The contribution of the $B$ mode to $T_{\text{vb}}$ is twice that of the $S$ mode, since CO$_2$ 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)], $T_{\text{vb}}=2450$ K, and $T_{\text{rot}}=350$ K. A similar estimation of $T_a$ in CO oxidation has previously been reported. The values of $T_a$, $T_{\text{vb}}$, and $T_{\text{rot}}$ are summarized as functions of desorption angle in Fig. 4(a). $T_{\text{vb}}$ decreases while $T_a$ and $T_{\text{rot}}$ increase as the desorption angle increases.

The different angular dependence between $T_a$ and $T_{\text{vb}}$ indicates that $A$ and $B$ modes differently couple to the translational mode in their excitation processes. When TS leaves the surface to become CO$_2$, the excess energy is partitioned into translational, vibrational, and rotational modes. The best...
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,

\[ \text{Fig. 4(d)} \]

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 \( T_{\text{rot}} \), low \( T_{\text{a}} \), and low \( T_{\text{b}} \). 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 \( T_{\text{ro}} \), high \( T_{\text{rot}} \), and low \( T_{\text{b}} \).

In the present work, \( T_{\text{a}} \) was higher than \( T_{\text{ar}} \), while in the previous work, \( T_{\text{a}} \) was higher than \( T_{\text{ar}} \) and \( T_{\text{b}} \) 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 \( T_{\text{ar}} \) 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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