

# A molecular beam scattering investigation of the oxidation of CO on Rh(111).

## II. Angular and velocity distributions of the CO<sub>2</sub> product

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Molecular beam and time of flight methods have been used to examine the angular distributions and velocity distributions of the CO<sub>2</sub> product molecules formed in the catalytic oxidation of CO on a Rh(111) single crystal in the surface temperature range 700–1000 K. The angular distribution was sharply peaked about the surface normal, and cannot be described by a simple  $\cos^n \theta$  expression. No temperature dependence was observed in the angular distribution over the range of temperatures studied here. Observed velocity distributions were clearly non-Maxwellian and had average translational energies in excess of those expected at the surface temperatures. Furthermore, the average velocity depended strongly on the desorption angle. Molecules desorbing along the surface normal had an average translational energy of  $\sim 8$  kcal/mol. The average energy decreased with increasing angle, reaching a value of  $\sim 4$  kcal/mol at an angle of 60°. All of the observed velocity distributions were narrower than Maxwellian distributions with the same average energies. Product velocity distributions did not appear to vary with surface temperature. The observed excess energies are believed to arise from the crossing of the activation barrier to reaction, with a fraction of the reaction energy being carried away from the surface by the product molecules.

### INTRODUCTION

Measurements of the angular, velocity, and internal energy distributions in the products of chemical reactions have contributed greatly to our knowledge of how such reactions occur. For reasonably simple gas phase processes, elegant crossed molecular beam experiments have led to a reasonable understanding of the reaction dynamics on the molecular level.<sup>1–3</sup> While such measurements are quite sophisticated experimentally, they are rather simple conceptually. Reactants are prepared in well defined initial states, made to collide in a controlled geometry, and the various parameters of the product molecule are investigated with state specific detection schemes. The experiment is carried out at sufficiently low pressures to ensure single collision conditions, so that the true nascent distributions formed in the reaction can be probed directly and unambiguously.

As the investigation of surface chemical processes has evolved in recent years, it has widely been hoped that a surface analog to the crossed beam experiment would be able to provide similar levels of insight into the molecular dynamics. Due to the complexity of the experiment, however, only a limited number of systems have been studied to date.<sup>4</sup> When compared with the gas phase situation, molecular beam studies of surface reactions are more difficult for two principle reasons. First, the need to maintain a clean surface means that the experiment must be performed under ultra-

high vacuum conditions, adding further to the technological difficulty of the measurement. Second, and more fundamentally, the product of a surface reaction is, by definition, formed in intimate contact with a reasonably efficient heat bath, the surface itself. This means that in general it is not possible to examine the true nascent distribution of energy in the product, as energy flow between the product and the solid surface may proceed quite rapidly, perhaps even as an essential step in a concerted reaction process. As such energy transfer occurs, information on the reaction dynamics is lost. At the present time, surface spectroscopic techniques do not offer sufficient sensitivity and time resolution to probe the adsorbed products as they are formed. Instead, the desorbed molecules must be interrogated. In the limit that the newly formed product molecules reach thermal equilibrium in the adsorption potential well prior to desorption, probing of the desorbed molecule in the gas phase cannot provide any information on the reaction itself.

If equilibration at the surface does occur, one generally expects the desorption angular, velocity, and internal energy distributions to be given by the Knudsen, Maxwell, and Boltzmann laws, respectively. Thus, a cosine angular distribution and translational and internal energy distributions characterized by the surface temperature are taken as evidence that the molecules were in equilibrium prior to desorption. While these "laws" are not rigorously true even for molecules at equilibrium, they do provide useful reference points. (For a thorough discussion of the applicability of the Knudsen, Maxwell, and Boltzmann laws in desorption processes, see Ref. 4.) For a few specific cases, however, sharply peaked angular distributions and substantial levels of internal and translational energy (in excess of the surface tem-

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perature) have been observed in the desorbed products of surface reactions, suggesting that some amount of dynamical information might survive the desorption process.

The oxidation of CO over platinum surfaces has been particularly well studied with regard to product energy distributions. The activation barrier for reaction lies roughly 20 kcal/mol above the gas phase CO<sub>2</sub> product, and this energy may be available for disposal into either translational and internal excitation of the product molecules or thermal excitation of the metal surface. Previous experiments indicate that the energy is actually divided among all of these alternatives. The onset of reaction causes a measurable increase in surface temperature, an effect which has been exploited to follow kinetic oscillations in the reaction rate under certain conditions.<sup>5</sup> Clearly this implies that a sizable fraction of the available energy is dissipated into the surface of the catalyst by coupling into lattice vibrations. Internal excitation of the CO<sub>2</sub> product molecules has also been observed by three groups,<sup>6-8</sup> and the degree of the observed excitation has been correlated with the surface coverage.<sup>6,7</sup> Translational energies of the desorbing molecules were measured by Becker *et al.*,<sup>9,10</sup> who reported non-Maxwellian velocity distributions with average energies well in excess of the surface temperature. In addition, sharply peaked angular distributions have been reported by several authors.<sup>10-12</sup> All of these results have been taken as an indication that the CO<sub>2</sub> product molecules do not equilibrate in the shallow physisorption well prior to desorption, but instead desorb more directly from a region of elevated potential energy.

All of the results mentioned above were obtained on platinum surfaces, primarily on either the (111) plane or on polycrystalline samples. Far less work has been done to date on the reaction over other catalysts such as palladium and rhodium, with only angular distributions having been reported. In an angularly resolved thermal desorption study, Matsushima *et al.*<sup>13</sup> found that the reaction on Rh(111) produced a sharply peaked angular distribution very similar to that obtained on Pt(111). For palladium, Engel and Ertl<sup>14</sup> found a cosine angular distribution in a molecular beam scattering experiment, while Matsushima<sup>15</sup> again found a very sharply peaked distribution in a thermal desorption experiment. The possibility of differences in dynamic behavior over these rather similar metal catalysts could offer an opportunity to gain a deeper understanding of the molecular reaction mechanism.

To examine this possibility further, we have undertaken a detailed examination of the CO oxidation reaction on a Rh(111) surface using a variety of molecular beam scattering techniques. Earlier we reported measurements of reaction rate constants by molecular beam relaxation spectrometry.<sup>16</sup> Here we present measurements of the angular dependence of both the flux and velocity distribution of the CO<sub>2</sub> product. To a large extent the results are quite similar to those obtained previously on platinum catalysts. In the present study, however, we have examined the product velocity distributions in more detail, including measurements of product velocity as a function of desorption angle. Such measurements can provide important new insights into the dynamics of reaction.

## EXPERIMENTAL

The molecular beam scattering apparatus has been described previously.<sup>10,16</sup> Very briefly, it provides two supersonic molecular beams which intersect at the surface of the target crystal. A rotatable quadrupole mass spectrometer is used to detect the product CO<sub>2</sub> molecules leaving the surface. One of the beams, CO in the present experiments, is modulated by a mechanical chopper producing a periodic flux of reactant molecules to the surface. This produces a product signal which is a function of time, and permits the determination of the time of flight of the CO<sub>2</sub> molecules over the 14.45 cm distance from the crystal to the detector. The angular resolution of the detector was approximately 1°.

A crucial limitation of the apparatus for the present purposes is the fact that the chopper modulates the incident reactant flux rather than the outgoing product flux. As explained in detail below, modulation of the incident CO beam leads to a signal which is the convolution of several factors, most notably the surface residence times of the CO and CO<sub>2</sub> species and the velocity distribution of the product. In an investigation of product velocity distributions, it would obviously be preferable to chop the outgoing molecules, as this would give a more direct measurement. By working at sufficiently high temperatures, however, we can reduce the surface residence times to a negligible level and extract accurate velocity distributions. The present geometry of the apparatus precludes the addition of an additional chopper between the crystal and detector.

## RESULTS

Figure 1 shows time of arrival waveforms for the CO<sub>2</sub> product molecules formed on an 800 K surface at desorption angles of both 0° and 60°. Clearly the curves differ, with the molecules desorbing along the surface normal arriving at the detector earlier than those desorbing 60° away from normal. This is in contrast with the situation at 550 K, where waveforms at 0° and 60° were indistinguishable (see Fig. 6 in Ref. 16). Our lower temperature measurements<sup>16</sup> of the activation energy and preexponential factor for the CO oxidation on Rh(111) predict a surface lifetime of 2 μs at a temperature of 800 K. This is considerably less than the dwell time of 6 μs per channel used to collect the data. As an upper bound to the possible surface lifetime, the surface residence time of a CO molecule on the clean Rh(111) surface at 800 K is about 8 μs,<sup>17</sup> which would still be only one channel in the present data. (On an oxygen covered surface the CO lifetime should decrease even further.) Based on these estimates, it seems clear that the drastic difference between the two waveforms cannot be due to residence times on the surface. The difference must be attributed to a difference in the velocity of the desorbed CO<sub>2</sub> product molecules at the two detection angles.

The obvious differences in the signal-to-noise ratio for the data at the two angles is due to the sharply peaked angular distribution of the product flux. Figure 2 shows the mass spectrometer signal for the modulated CO<sub>2</sub> product as a function of desorption angle from the surface normal. (Note that this signal is number density, not flux. Examples of the

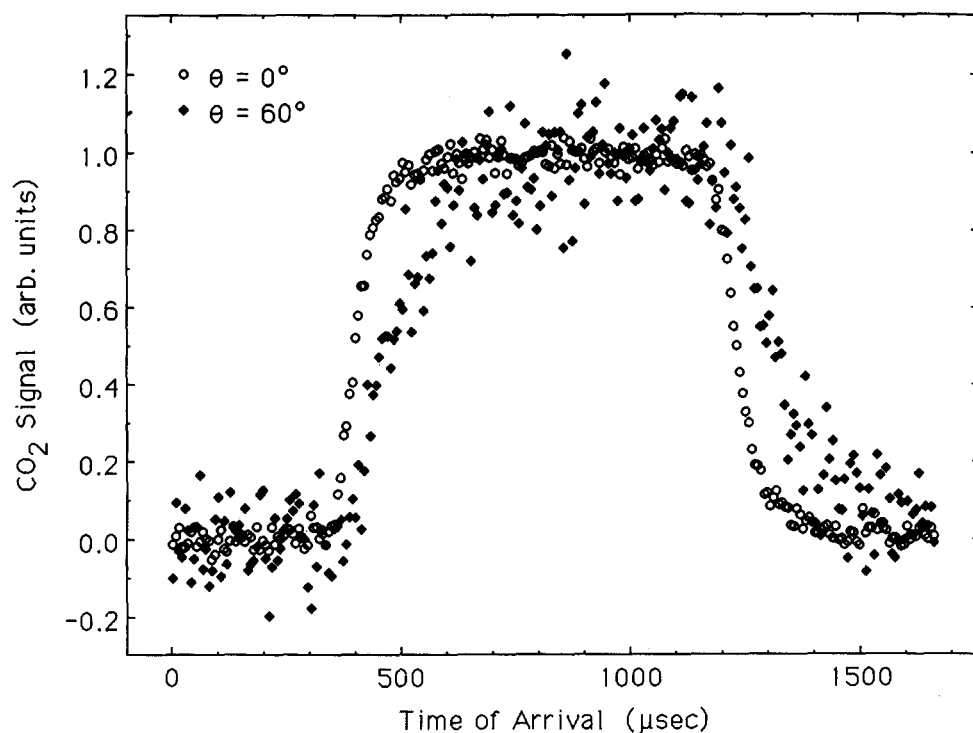


FIG. 1.  $\text{CO}_2$  time of arrival waveforms measured at the indicated desorption angles. The surface temperature was 800 K, the chopping frequency was 600 Hz, and the dwell time for each data point was  $6 \mu\text{s}$ . The difference between the two waveforms is due to the angular dependence of the product velocity distribution. (Note that the two waveforms have been normalized to the same amplitude in order to point out the differences in shape.)

correction for the angularly dependent velocity distributions are also shown in the figure, and will be discussed in the next section.) The distribution is clearly peaked very sharply along the surface normal. As in the previous paper,<sup>16</sup> we have fit the distribution with a two-channel expression originally used by Segner *et al.*<sup>12</sup>:

$$I(\theta) = \alpha \cos^n \theta + (1 - \alpha) \cos \theta. \quad (1)$$

The implications of this form will be discussed below. Be-

cause of the sharpness of the distribution, it is rather difficult to obtain good time of flight waveforms at large angles from the surface normal. In Fig. 1, for example, the data for  $\theta = 0^\circ$  were collected in about 3 h, while those for  $\theta = 60^\circ$  required nearly 24 h of data collection. Still, the waveform taken along the surface normal obviously has much better statistics. Practical considerations and concern over the stability of the catalyst over very long measurement times dissuaded us from extending the data collection times any further. Similarly, we were unable to obtain meaningful data for desorp-

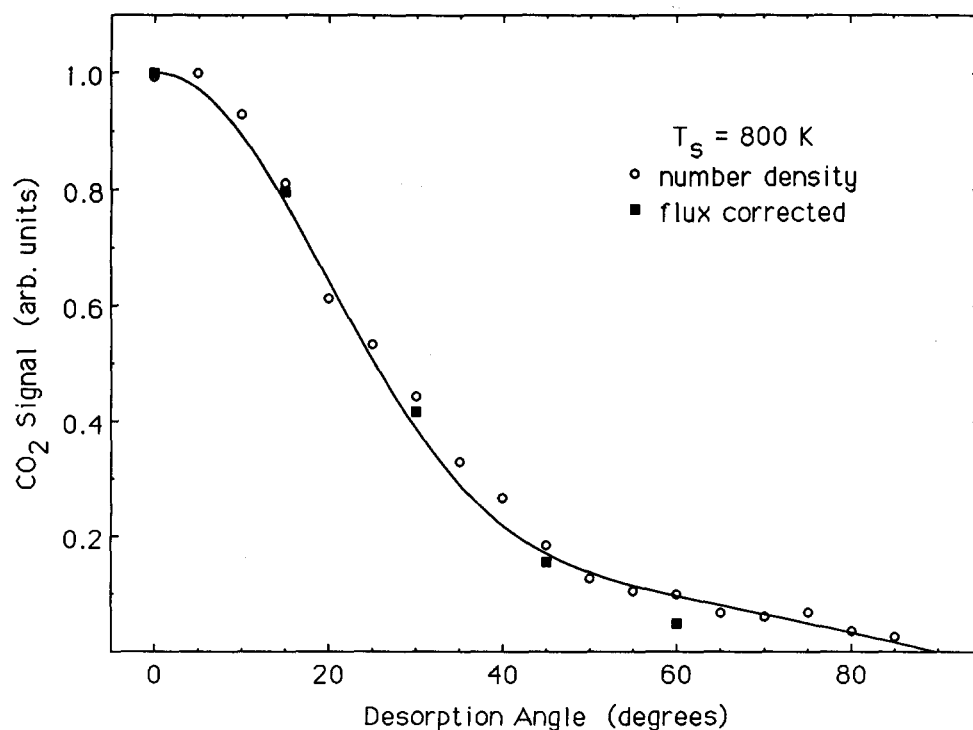


FIG. 2. Product  $\text{CO}_2$  angular distribution at a surface temperature of 800 K. The circles indicate the mass spectrometer signal, which is sensitive to number density, while the solid squares show the flux weighted signal, corrected for the angularly varying velocities. The solid line is a best fit of Eq. (1) to the number density data, and corresponds to values of  $n = 9$  and  $\alpha = 0.81$ . Within the range of 700–1000 K considered here, the angular distribution was not sensitive to surface temperature.

tion angles greater than  $60^\circ$  from normal, where the signal levels drop off even further.

As explained previously,<sup>16</sup> the signal measured in these experiments is a convolution of several factors, including the chopper gating function, incident beam velocity distributions, surface lifetimes (of CO and CO<sub>2</sub>), and outgoing product velocity distributions. For the present purposes, it is the product velocity distribution which is of interest, and the remaining contributions are either known or can reasonably be neglected. The chopper function is simply a square wave for all of the data presented here, and the incident beam velocity distribution can be measured directly by rotating the detector into the path of the beam. The surface lifetimes have been determined accurately in the lower temperature range (500–600 K), and we will assume that the parameters determined can be extrapolated to the higher temperatures considered here. While this assumption might be regarded with some caution, it is of little significance since the residence times must be on the order of the channel time and therefore cannot appreciably influence the waveforms. Attempts to extract the velocity distribution function directly by deconvoluting the various other contributions from the experimental data were unsuccessful because the deconvolution process is extremely sensitive to noise in the data. It was therefore necessary to use a nonlinear fitting process to determine the product velocities.

We have chosen to assume that the velocity distribution of the product CO<sub>2</sub> molecules is of the form<sup>4</sup>

$$F(v) = Nv^3 \exp\left[-\left(\frac{v-v_0}{\alpha}\right)^2\right]. \quad (2)$$

Such a distribution is frequently used to describe a super-

sonic molecular beam, and is defined by the two parameters  $V_0$  and  $\alpha$ . ( $N$  is a normalization constant.) The former is referred to as a stream velocity, and the latter describes the width of the distribution. Note that for  $V_0 = 0$ , this becomes a Maxwellian distribution with a temperature given by

$$T = \frac{m\alpha^2}{2k}. \quad (3)$$

This allows a distribution of the same form to describe either thermalized molecules or molecules with excess translational energy. For a given choice of  $V_0$  and  $\alpha$  a waveform is synthesized by convolving the trial velocity distribution with the chopper function, incident beam distribution, and surface residence time distribution. The resulting waveform can be compared to the data, and the process performed iteratively to achieve a least-squares fit. The fitting was done using a multidimensional simplex procedure.<sup>18</sup> Results of such fits are shown as the solid lines in Fig. 3, and the best fit parameters are listed in Table I.

Data obtained at a variety of surface temperatures and desorption angles have been fit in this way. Figure 4 shows the best-fit velocity distributions obtained for CO<sub>2</sub> molecules formed at a surface temperature of 800 K and desorbing at three different angles, along with the distribution expected for molecules leaving an 800 K surface in thermal equilibrium. (Such an equilibrated distribution at 800 K has a mean kinetic energy of 3.2 kcal/mol.) Two important results are readily apparent from this figure. First, the velocity distribution depends strongly on desorption angle, with molecules desorbing along the surface normal being considerably faster than those desorbing at more glancing angles. Second, even at an angle of  $60^\circ$  from the surface normal the product mole-

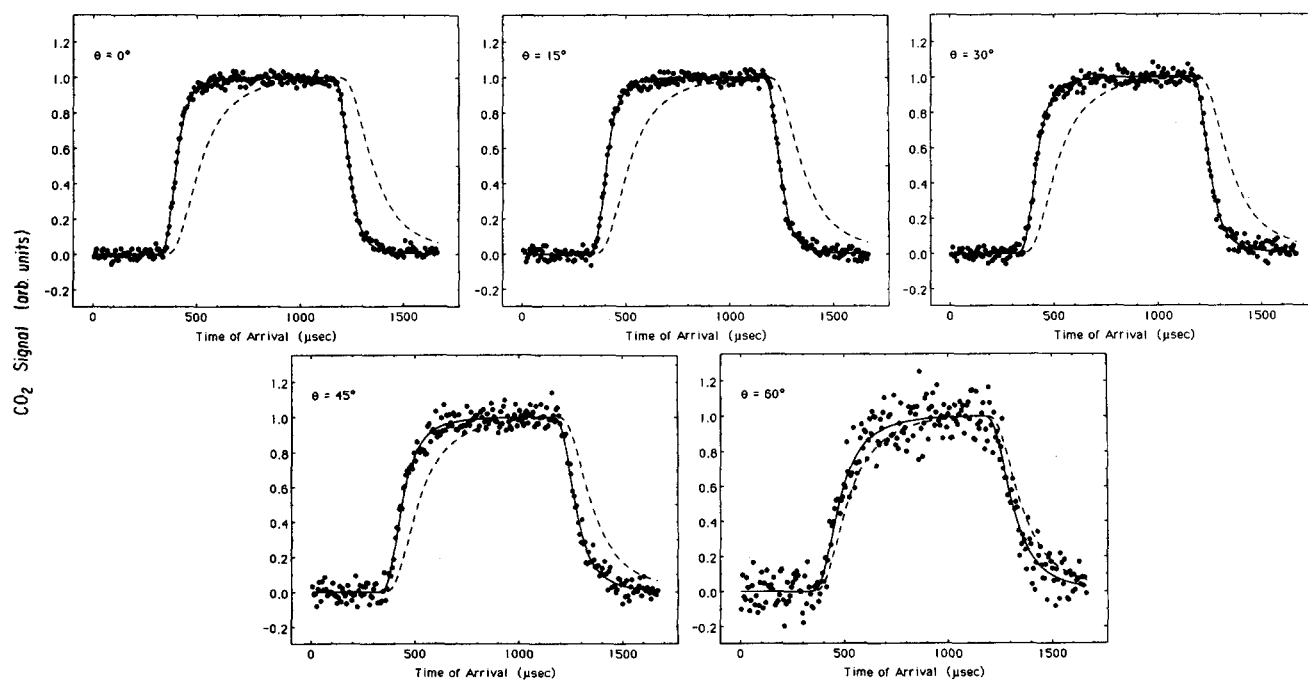


FIG. 3. Time of arrival waveforms for the indicated desorption angles at a surface temperature of 800 K are shown along with best fits obtained using the convolution procedure described in the text. The fit parameters for each waveform are given in Table I. Also shown by the dashed line in each panel is the waveform which would result if the product desorbed with a Maxwellian velocity distribution at the surface temperature.

TABLE I. Parameters describing best-fit velocity distributions for CO<sub>2</sub> molecules desorbing from an 800 K Rh(111) surface.

Angle (deg)	$V_0$ (cm/s)	$\alpha$ (cm/s)	$\langle V \rangle$ (cm/s)	$\langle E \rangle$ (kcal/mol)
0	$8.7 \times 10^4$	$5.2 \times 10^4$	$1.2 \times 10^4$	8.5
15	$8.5 \times 10^4$	$5.1 \times 10^4$	$1.2 \times 10^4$	8.1
30	$7.3 \times 10^4$	$5.4 \times 10^4$	$1.1 \times 10^4$	7.5
45	$4.9 \times 10^4$	$5.7 \times 10^4$	$1.0 \times 10^4$	6.1
60	$2.3 \times 10^4$	$5.4 \times 10^4$	$8.4 \times 10^3$	4.3

cules have velocities considerably in excess of those corresponding to a Maxwellian distribution at the surface temperature.

The average translational energy is related to the velocity distribution by

$$\langle E_t \rangle = \frac{1}{2} m \langle v^2 \rangle = \frac{1}{2} m \int_0^\infty v^2 F(v) dv \quad (4)$$

which can be evaluated by numerical integration. Figure 5 shows the average energies obtained in this fashion for a variety of desorption angles and surface temperatures. The translational energy is again seen to drop off with increasing angle from the surface normal. In the range of angles measured, the translational energy appears to vary as the cosine of the angle from the surface normal. Clearly, this cosine dependence must be regarded with caution due to the limited data available. In particular, the data do not show whether the mean translational energy continues to decrease below the expected thermal value of  $2kT$  as the desorption angle increases towards  $90^\circ$ . It was not possible to obtain data at more glancing angles ( $\theta > 60^\circ$ ), because the signal level at such angles was too low. The translational energy of the product CO<sub>2</sub> does not appear to depend on surface temperature, although only a fairly narrow range of temperatures is accessible. Below 700 K the surface lifetime of adsorbed CO contributes significantly to the shape of the observed time of

arrival waveform, while above 1000 K there is simply not enough product yield to make reasonable measurements. In considering their results on vibrational excitation in CO<sub>2</sub> produced on platinum, Mantell *et al.*<sup>7</sup> suggested that the translational energy might be decreasing with increasing surface temperature. No evidence for such an effect is seen, either here or in the data of Becker<sup>9,10</sup> for the reaction on platinum.

## DISCUSSION

The time of arrival waveforms clearly show that the velocity distribution in the product CO<sub>2</sub> molecules varies as a function of the desorption angle. Since the channel time used to collect the data is greater than the residence time of adsorbed CO at the temperatures considered here, the observed effects cannot be attributed to surface lifetimes. Only a variation in the product translational energies can explain the data.

Several comments on the fitting procedure employed to extract the velocity distribution are in order. Best fits to all of the data were obtained with non-Maxwellian distributions, although the form of Eq. (2) clearly allows for the possibility of a thermal distribution in the case that  $V_0 = 0$ . Attempts to fit the data with a Maxwellian distribution of velocities (i.e., restricting  $V_0$  to 0) failed to produce satisfactory fits. Similarly, the possibility that the actual distribution could be bimodal was considered by running fits in which two distributions of the form of Eq. (2) in varying ratios were used. In all cases the fitting routine set the contribution of the second distribution to zero, giving the best fit for a single distribution.

The issue of bimodality in the velocity distribution is important because of the form of the angular distribution of the desorbing molecules. We have again followed the example of Segner *et al.*<sup>12</sup> and used a two channel model [Eq. (1)] to describe the observed distribution. In originally choosing this model, those authors suggested that the cosine term was due to molecules which had thermalized at the surface while the sharply peaked term was due to molecules desorbing more rapidly. As stated previously,<sup>16</sup> we feel that this interpretation of the data is not necessarily correct. Since there is no *a priori* reason why the desorption flux should be given by  $\cos^n \theta$ , the separation into two terms [Eq. (1)] does not need to imply two desorption channels. This idea is reinforced by the current results. Assuming that the interpretation of Segner was correct, we would expect those molecules which were directly desorbed ( $\cos^n \theta$  term) to be more energetic than those in the thermalized cosine channel. This would produce a bimodal velocity distribution, at least at those angles where both terms contribute appreciably to the angular distribution. Furthermore, we would expect those molecules desorbing in the cosine channel to exhibit a Maxwellian velocity distribution at the surface temperature. As seen in Fig. 4, the data do not support these assumptions. No bimodal distributions were observed under any of the conditions investigated. Even at an angle of  $60^\circ$  from the surface normal, where the cosine channel in Eq. (1) dominates the angular distribution, the observed velocity distributions are non-Maxwellian and the translational energy is in excess of

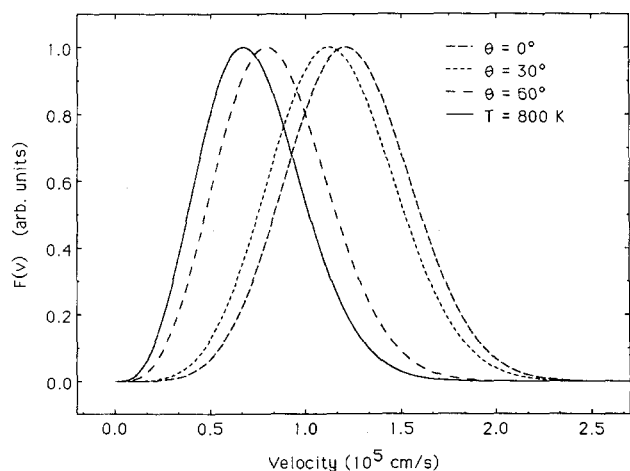


FIG. 4. The velocity distributions obtained from best fits to waveforms obtained at the indicated desorption angles and a surface temperature of 800 K are shown. The solid line shows the distribution expected for molecules equilibrated with the surface at 800 K.

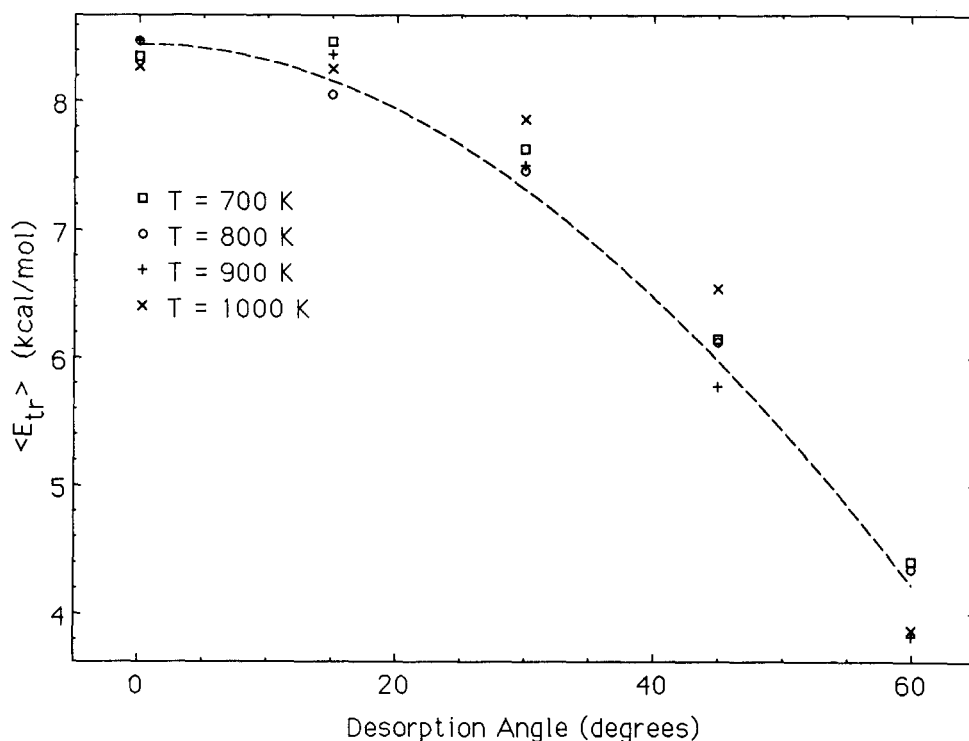


FIG. 5. Average translational energies obtained from integrating the best-fit velocity distributions are shown as a function of desorption angle and surface temperature. Over the temperature range accessible here, no systematic variation of translational energy with surface temperature is seen. The translational energy decreases sharply as the desorption angle increases, falling from  $\sim 8.4$  kcal/mol at  $0^\circ$  to  $\sim 4$  kcal/mol at  $60^\circ$ . The dashed line is simply  $\cos \theta$  scaled to fit the data. While this curve gives a reasonable fit to the data, no explanation of this dependence is currently available. Data at larger (more glancing) desorption angles could not be obtained because of low signal levels.

the surface temperature. Simulated time of flight waveforms in which a fraction [given by  $(1 - \alpha)$  in Eq. (1)] of the molecules were assumed to be fixed at thermal velocities consistently gave poorer fits to the data than those using a single nonthermal velocity distribution. As in our previous paper,<sup>16</sup> none of the current results seems to indicate that the desorption flux is divided into two distinct processes.

Since we have determined the product velocity distributions as a function of desorption angle, we can transform the signal from the mass spectrometer, which is sensitive to the number density of product molecules, into a properly flux weighted quantity. Since the number density varies inversely with velocity, the raw mass spectrometer signal will tend to undercount the faster molecules. Because the velocity is highest along the surface normal, this means that the distribution measured by the mass spectrometer will be less sharply peaked than the correct flux distribution. In Fig. 2 we have included flux corrected data points for those angles at which the velocities have been determined. The overall effect is rather minor. A fit of Eq. (1) to the flux corrected data points gives values of  $\alpha = 0.90$  and  $n = 7$ , compared to the values of 0.81 and 9 obtained using the raw data. Again, the lack of data at more glancing angles limits the interpretation of the flux corrected data. The fraction  $(1 - \alpha)$  in the cosine channel is determined primarily by the data point at  $60^\circ$ , which is the least accurate of the points because of the low signal at large angles. Within the accuracy of the data, however, it still appears that the two channel form of Eq. (1) gives a better fit to the data than can be achieved with a simple  $\cos^n \theta$  expression.

Qualitatively, the excess energy in the  $\text{CO}_2$  product can be understood by considering the potential energy diagram of Fig. 6. The high translational energies measured in these

experiments, as well as the internal excitations which have been reported previously, can be viewed as the retention in the products of at least a portion of the reaction exoergicity. In terms of Fig. 6, this means that the  $\text{CO}_2$  molecules are

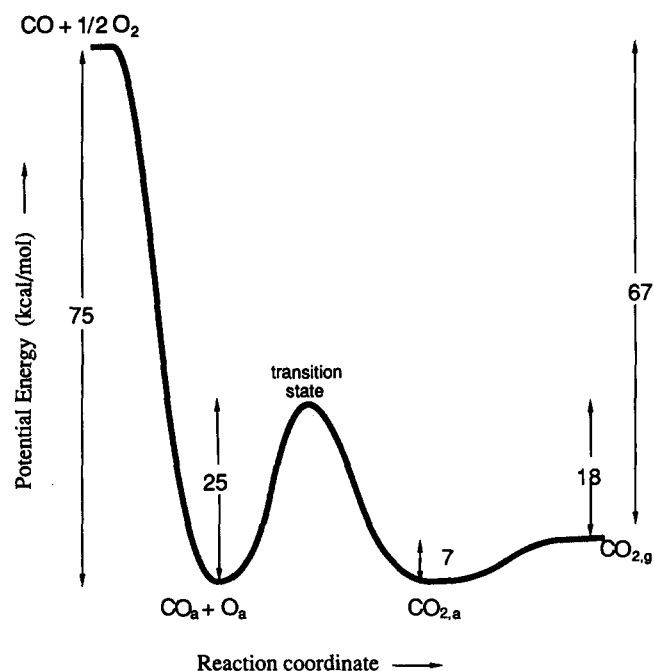


FIG. 6. A highly schematic one-dimensional potential energy diagram is shown for the oxidation of CO on Rh(111). While such a diagram is clearly an oversimplification it can be useful in discussing some qualitative aspects of the reaction dynamics. All energies are given in kcal/mol. The transition state can be seen to lie some 18 kcal/mol above the energy of free gas phase  $\text{CO}_2$ , and the excess energy observed in the product represents the retention of a portion of this energy in the desorbed molecule.

evolved into the gas phase directly from a region of higher potential energy without first thermalizing in the shallow physisorption potential well. (In scattering experiments using an incident CO<sub>2</sub> beam, we have measured the depth of this well as  $\sim 7$  kcal/mol.) Further insight can be obtained by considering the configuration of the adsorbed reactants and the product CO<sub>2</sub> molecule. The reactant CO molecule is bound to the Rh(111) surface with the carbon end down and the molecular axis normal to the surface,<sup>19</sup> whereas the O<sub>2</sub> molecule adsorbs dissociatively as O<sub>a</sub> atoms. This means that in the reactants an O–C–O bond angle of 90° exists, as opposed to the 180° bond angle in the product. The C–Rh bond length in adsorbed CO is approximately 1.86 Å.<sup>20</sup> On the basis of molecular orbital calculations,<sup>21</sup> CO<sub>2</sub> has been predicted to adsorb on Pt(111) as a linear molecule with its axis perpendicular to the surface. The preference for perpendicular vs parallel orientation was attributed to stabilization of the CO<sub>2</sub>  $\sigma_p$  lone pair orbital because of overlap with a metal orbital of *s* and *d* character.<sup>21</sup> Similar bonding would be expected on Rh(111). Since the physisorption bond between CO<sub>2</sub> and the surface is largely a van der Waals interaction, an equilibrium separation of a few angstroms would be expected. This means that in moving from the reactant geometry towards products, the carbon atom must move away from the surface at the same time as the O–C–O bond angle moves from 90° towards 180° and the second C–O bond forms. The bond bending and forming motions might be expected to produce vibrational excitations in the nascent CO<sub>2</sub> molecule, while the motion of the carbon atom away from the surface is equivalent to translation in the product. Assuming that the transition state along the reaction pathway of Fig. 6 corresponds to a configuration in which the carbon–rhodium internuclear distance is shorter than that expected for adsorbed CO<sub>2</sub>, then one would expect the repulsive part of the Rh–CO<sub>2</sub> interaction potential to push the molecule away from the surface. This repulsion can qualitatively explain the high translational energy seen in the product CO<sub>2</sub>, as well as the sharply peaked angular distribution.

One motivation for the present study on Rh(111) was the difference in the angular distributions observed previously on Pt(111) and Pd(111). The current results are very similar to those obtained on platinum, while on palladium a cosine angular distribution was reported. A possible explanation of this difference may be suggested by the sort of molecular orbital arguments presented above. Recent experiments on iron<sup>22</sup> and nickel<sup>23</sup> surfaces indicate the existence of an adsorbed CO<sub>2</sub> species lying nearly flat, possibly in a bent geometry. If the preferred orientation of CO<sub>2</sub> on palladium is with its molecular axis parallel to the surface, then the incipient molecule might be subjected to considerably weaker repulsive forces, allowing equilibration at the surface and leading to the observed cosine angular distribution.

Nonthermal velocity distributions in molecules produced in surface reactions have been observed previously in other studies.<sup>4</sup> By far the most thoroughly examined system in this regard is the recombinative desorption of H<sub>2</sub> from metal surfaces. In a series of experiments involving permeation through membranes, Comsa and various co-workers have shown that distinct “fast” and “slow” distributions of

desorbing molecules are produced.<sup>4</sup> The fast molecules showed a sharply peaked angular distribution, while the slow ones desorbed in a cosine distribution. Through the use of cross-correlation time of flight methods,<sup>24</sup> the two distributions have been clearly resolved. In an earlier study of CO oxidation on platinum, Becker *et al.*<sup>9</sup> measured non-Maxwellian velocity distributions with energies well in excess of those corresponding to the surface temperature. (Note that although Ref. 9 uses Kelvin as an energy unit, the observed distributions are definitely non-Maxwellian.) Becker also observed that the velocity distribution was a function of desorption angle,<sup>9,10</sup> with faster molecules desorbing along the surface normal, although this result was not examined in detail. For both these cases, sharply peaked angular distributions and high translational energies have been reported, with the translational energy depending on the desorption angle. In contrast to these observations, Ceyer *et al.*<sup>25</sup> reported that D<sub>2</sub>O produced in the oxidation of deuterium on a Pt(111) surface desorbed in a cosine angular distribution but translationally colder than the surface temperature. Also, the translational energy did not appear to depend on desorption angle in this case.

In considering such results, several models have been proposed as explanations for the origin of the nonthermal distributions and peaked angular distributions. The oldest and simplest of these is the Van Willigen model<sup>26</sup> in which a molecule must overcome a one-dimensional potential barrier to escape from the surface. While such a model can readily account for a peaking of the angular distribution along the surface normal, it predicts that the average velocity of the desorbed molecules should increase with increasing angle from the surface normal. This is in disagreement with the experimental results presented here. Comsa<sup>27</sup> has discussed a modification of this model to include “holes” in the barrier. While this model is not intuitively satisfying, it was able to roughly account for the distributions observed in the H<sub>2</sub> permeation experiments. An important distinction between those results and the present ones, however is that the H<sub>2</sub> velocity distributions were found to be bimodal, with distinct fast and slow components. The “barrier-with-holes” model naturally produces such a separation, as some molecules must overcome the barrier while others pass through the holes. In the current experiments, however, no evidence of bimodality has been seen.

The most interesting result of the present study is the dependence of the translational energy on the desorption angle (Fig. 5). The observed effect cannot be explained by any of the models cited above. Translational energy was seen to decrease with increasing angle from the surface normal, in direct conflict with the predictions of the simple Van Willigen model. No evidence of bimodality was found, as expected for the barrier-with-holes model. The angular dependence of the translational energy could, perhaps, be produced by extending the barrier-with-holes model to include a distribution of barrier heights. (This was actually the original motivation for Comsa’s proposal of the barrier with holes.) Doyen<sup>28</sup> proposed a quantum mechanical model which predicted an angular variation in the mean translational energy for molecules desorbing in an angular distribu-

tion given by  $\cos^n \theta$ , and a similar model has more recently been described by Wilsch *et al.*<sup>29</sup> For an angular distribution described by  $\cos^{n+1} \theta$ , the mean energy for particles desorbing at an angle  $\theta$  was predicted to be<sup>28</sup>

$$E(\theta) = kT\{(2 + n/2)\cos^2 \theta + 2 \sin^2 \theta\}. \quad (5)$$

This gives a maximum energy of  $(2 + n/2)kT$  along the surface normal and decreases to the thermal value of  $2kT$  as  $\theta$  goes to  $90^\circ$ . If we were to simply neglect the second term of Eq. (1) and approximate the angular distribution by  $\cos^7 \theta$ , Eq. 5 would give a mean energy of  $5kT$ . For a surface at 800 K, this gives energies of 8.0 kcal/mol at  $\theta = 0^\circ$  and 3.2 kcal/mol at  $\theta = 90^\circ$ , in reasonably good agreement with the experimental data. While the predicted variations in energy as a function of angle are apparently consistent with the experimental results, several discrepancies exist. First, applying Doyen's model to an angular distribution of the form of Eq. (1) would again lead to a bimodal velocity distribution, since those molecules desorbing in the cosine channel would still be expected to show a thermal distribution with  $E_i = 2kT$ , independent of angle. Furthermore, the model predicts a temperature dependence for the energies, whereas none was found experimentally. Finally, it is not clear from the data if the energy actually does level off at the expected thermal value as the desorption angle approaches  $90^\circ$ . In the  $H_2$  permeation experiments cited above, for example, Comsa found that molecules desorbing at glancing angles were considerably slower than thermal.<sup>4</sup> More detailed measurements may be required to assess the applicability of these models.

It is very important to remember that the results in Fig. 5 are only for *translational* energy, and not for the total energy carried away in the  $CO_2$  molecule. Previous experiments have demonstrated that the product molecules formed in CO oxidation on platinum surfaces carry substantial amounts of energy in vibrational and rotational excitations.<sup>6,7</sup> In light of the similarity in the overall energetics of reaction, as well as the similar angular distributions and translational energies reported here, we expect that the  $CO_2$  product formed on the rhodium surface will also be internally excited. No information is currently available on any possible angular dependence in this internal excitation. The angularly resolved state specific detection of  $CO_2$  at the small fluxes produced in this type of experiment is a very difficult measurement which we are not currently able to perform. Without such a measurement, the possibility remains that the internal energy in the product molecules may also depend on desorption angle, perhaps in such a way that the total energy carried away from the surface (translation + vibration + rotation) may be independent of angle. One could imagine, for example, that molecules desorbing at more glancing angles might carry significant amounts of rotational or vibrational energy as compared to those desorbing along the surface normal. Changes in the critical configuration of  $CO_2^\ddagger$  as a function of final desorption angle might lead to such a result. If such a dependence exists, then the fraction of the reaction exoergicity deposited into the molecule (as opposed to into the surface) might remain constant as a function of desorption angle in spite of the results shown in Fig. 5. In this case the

angular dependence in translational energy seen here would reflect variations in the partitioning of energy within the desorbed product molecule rather than between the molecule and the surface. To address this question it will be necessary to measure angularly resolved internal energy distributions in the product molecules. Such angularly resolved state specific velocity distributions could perhaps be obtained, albeit with great difficulty, by measuring Doppler profiles in infrared emission or absorption experiments.

There has been a considerable amount of controversy in the literature regarding the possibility of dissociative adsorption of  $CO_2$  on rhodium surfaces.<sup>30,31</sup> Since this represents the inverse of the oxidation reaction, the two processes are related by microscopic reversibility, and the present data may have some relevance to the discussion. Specifically, it would seem that the dissociation of  $CO_2$  into CO and O must be strongly activated. Furthermore, the sharply peaked angular distribution and the high translational energy seen in the reaction product should also be observed in the dissociative sticking process. That is, the sticking probability should be significantly enhanced for molecules incident along the surface normal, and translational energy might be expected to be fairly effective in promoting dissociation.

We made a brief attempt to examine this possibility by looking for dissociative sticking of fast  $CO_2$  molecules. A small amount of  $CO_2$  was seeded in a beam of helium to produce translational energies near 20 kcal/mol, well above those observed in the reaction product and roughly equal to the adsorption barrier height expected on the basis of Fig. 6. The Rh(111) surface at 300 K was exposed to the seeded beam. At this temperature, physisorbed  $CO_2$  should not stick to the surface, but adsorbed CO and O should be fairly stable. The specularly reflected helium carrier gas was used to monitor surface coverage. It has been well established that helium reflectivity from a close packed metal surface is extremely sensitive to the presence of small amounts of adsorbates.<sup>32</sup> No decay in the reflectivity was observed, indicating that no appreciable dissociation of the incident  $CO_2$  occurred. It is possible that vibrational energy may be important in promoting any dissociative adsorption of  $CO_2$ , since stretching motion should be strongly involved in the reaction coordinate for dissociation. The seeded beam used produces internally cold molecules with high translational energies, whereas we believe that the molecules produced in the CO oxidation reaction (and hence those most likely to adsorb dissociatively) are both internally and translationally excited. Microscopic reversibility arguments suggest that ensembles of molecules similar to those produced by the CO + O reaction should be effective in promoting dissociative adsorption of  $CO_2$ .

## CONCLUSION

We have used modulated molecular beam techniques to measure the velocity distribution in the  $CO_2$  product formed in the catalytic oxidation of CO on a Rh(111) surface. The mean translational energy depends strongly on the desorption angle, and does not appear to depend on the surface temperature. In the surface temperature range from 700–1000 K, molecules desorbing along the surface normal were

found to have translational energies of roughly 8 kcal/mol, while those desorbing at an angle of 60° from normal had energies around 4 kcal/mol. At all angles the observed velocity distributions were markedly non-Maxwellian, as the widths were much narrower than those of thermal distributions with the same mean energies. The excess energy is believed to arise from the crossing of the activation barrier to reaction, with the product molecule carrying a fraction of the reaction energy away from the surface. The results, particularly the angular variation of the translational energy, are at odds with several models which have been proposed in the literature for other systems.

The angularly resolved velocity measurements presented here represent another step in the assembly of a growing array of information on energy disposal in the CO oxidation reaction on platinum and rhodium surfaces. Classical trajectory calculations have already had some success in modeling the vibrational energy distributions produced in the reaction on platinum.<sup>33</sup> It is our hope that this newest piece of the puzzle might contribute to improvements in such calculations for this model reaction system. Although at this point there is probably more known about the dynamics of this reaction than any other bimolecular surface process, important information is still lacking. Particularly, many questions would be answered by angularly resolved measurements of the internal energies of the CO<sub>2</sub> product. While this will be a significantly more difficult measurement, the additional information could be pivotal in developing an accurate model of essential features of the reaction potential energy surface.

In combination with the previous paper,<sup>16</sup> this work demonstrates the versatility of molecular beam methods as a probe of surface chemistry. At relatively low surface temperatures, the reaction time constants can be forced into the millisecond time scale. This allows the study of kinetic and mechanistic aspects such as rate constants and reaction branching ratios. At the higher temperatures used in the present work, we are able to isolate processes occurring on a much shorter time scale and examine aspects of the reaction dynamics.

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