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Microscopic CO Diffusion on a Pt(111) Surface by Time-Resolved Infrared Spectroscopy

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A new technique, combining a pulsed supersonic molecular-beam source and time-resolved surface infrared spectroscopy, has been devised to measure the microscopic diffusion of molecules at surfaces. Following a rapid dose of a periodically stepped Pt(111) crystal face to a low total coverage of CO (~0.006 monolayer), the time evolution of CO molecules migrating from terrace to step sites was monitored with a temporal resolution as fast as 5 msec. When compared with a simple kinetic model, the data reveal statistical microscopic hopping rates for CO diffusion on the (111) plane over the $T=95-195$ K range investigated.

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The motion of molecules at surfaces is central to the kinetics of adsorption, desorption, and surface chemical reactions, and to the formation of equilibrium configurations. The significance of this mechanism to every aspect of gas-surface interactions has motivated considerable experimental effort: Field-emission[1] and field-ion[2] microscopies have provided direct evidence for site-to-site hopping mechanisms and yielded quantitative measures of microscopic diffusion; other approaches, such as Auger-electron spectroscopy[3] and laser-induced desorption,[4] have related macroscopic displacements to microscopic diffusion processes. These pioneering studies, however, exhibit experimental limitations that restrict the scope of surface diffusion measurements. Measurement conditions for the microscopic probes are generally limited to small crystal faces of refractory materials under high-field conditions. Macroscopic probes such as Auger-electron spectroscopy and laser-induced desorption are highly dependent on the microscopic perfection of the surface because they cannot differentiate between molecules trapped at defects and adsorbed on low-index planes. Unfortunately, the best surfaces have surface defects (e.g., steps and kinks) separated by distances less than 500 Å. Since these defects usually bind adsorbed molecules more strongly than the low-index plane terraces, the macroscopic diffusion of molecules may well be dominated by the defects, particularly at low coverages.

We have developed a new technique, synchronizing a pulsed supersonic molecular-beam doser with surface infrared measurements, to record the microscopic diffusion of molecules at surfaces. The method is based upon the observation that both the binding energies and the vibration frequencies are different for molecules adsorbed on low-index planes and at defects (e.g., steps), because of the different coordinations of the two sites.[5] Thus, if it can overcome the barrier(s) to diffusion, an isolated molecule initially adsorbed on a low-index plane will migrate to a more tightly binding step, exhibiting a shift in its characteristic vibrational spectrum. The microscopic information is afforded by the ability of infrared spectroscopy to measure such small frequency shifts, thereby differentiating between molecules adsorbed on low-index planes and at defects. The technique, applicable to both metal and semiconductor surfaces, is also *chemically specific* and can, in principle, measure the time evolution of *several* different molecular species simultaneously.

In this Letter we demonstrate this approach by monitoring the temporal evolution of the vibrational spectrum for low CO coverage [$\theta=0.006$ monolayer (ML), where 1 ML = 1.5×10^{15} CO/cm^2] upon fast dosing (~600 μs) of a surface. From these measurements, absolute number distributions of CO on (111)-terrace and at step sites are extracted over wide temporal ($5\times10^{-3}\,\mathrm{s}<t<3\times10^{4}\,\mathrm{s}$) and thermal ($95<T<195$ K) ranges. For a quantitative interpretation of the data, we have relied upon a simple kinetic model with a minimum of adjustable parameters. This yields a hopping rate which is well fitted by an Arrhenius form with an activation barrier to diffusion $\Delta E_t=4.4$ kcal/mol (0.19 eV) and the associated prefactor $A_t=8\times10^{9}\,\mathrm{s}^{-1}$.

The critical experimental aspects of this method are (1) the timing and duration of the gas deposition at the surface with respect to the time-resolved infrared detection, (2) the sample preparation and characterization, and (3) the broad thermal range covered.

Fast and precise dosing of the surface was achieved by a pulsed molecular-beam source[6] that introduced a uniform flux of CO over the whole sample (2.5×1 cm^2) in a 600-μs time window, without degrading the pressure in the UHV chamber. The timing of the one-shot gas pulse with respect to the fast scanning interferometer was such that the separation between the fall of the gas pulse at the sample and the center of the first interferogram was set at 5.4, 10.8, and 22 ms for 16-, 8-, and 4-cm^{-1} apodized resolution, respectively. Subsequent interferograms were separated by 22-, 32-, and 55-ms time intervals, respectively. Since change occurs on a nonlinear time scale, however, only the first forty interferograms were accumulated at these rapid time intervals. At longer times, the data acquisition rate was reduced according to a power form to facilitate data handling.

The sample was a platinum (111) single crystal "misscut" by 1.7° about the $\langle\bar{1}2\bar{1}\rangle$ axis. Low-energy electron diffraction showed that the surface exhibited a regular array of monatomic steps along $\langle\bar{1}10\rangle$ separated by 29 atoms (80.5 Å). In short, the surface is Pt(29, 28, 27). This corresponds to step edges cut across next nearest neighbors. Although CO binds exclusively to atop sites at lower coverages ($\theta \leq 0.15$ ML CO),[7] the stepped surface morphology gives rise to three distinct top binding sites. At $T=125$ K the terrace band appears at 2087.5 cm^{-1}, and two additional step bands appear at 2057.6 and 2067.6 cm^{-1}. The narrow linewidths of all three modes (<6 cm^{-1} at $T=100$ K) are an indication of homogeneous sites. The assignment of the lower-frequency features to step sites, as opposed to defects or islanded species, was ascertained from coverage-dependent equilibrium and time-resolved infrared measurements. However, only one step site ($\tilde{\nu}=2057.6$ cm^{-1}) appears to be kinetically accessible in the time-resolved studies at the shorter times ($t<3\times10^5$ ms) relevant for diffusion across terraces.

Since the number of step sites is only 3.5% of the total number of terrace sites, and the packing density is determined to be considerably lower than unity, sample cleanness on a $<0.05\%$ ML scale is critical. As a precaution against introducing inhomogeneous surface defects, a cleaning procedure was adopted that did not involve sputtering. Initially the Pt sample was heated to 1270 K in 5×10^{-7} Torr O_2 for periods of 1 h, followed by cooling to $T=100$ K and flashing to 1370 K in vacuum (10^{-10} Torr). Twenty such cycles were repeated.

Subsequently, before each measurement a minimum of one cleaning cycle was performed with an oxygen-bake duration of 30 min. Also prior to each run, Auger measurements taken with a single-pass cylindrical-mirror analyzer indicated that impurity levels for Ca, C, Si, and O were below the limits of detectability ($<0.1\%$ ML at the surface). As noted above, our sample cleanliness requirements were beyond the sensitivity of our Auger measurement. In fact, the absolute infrared intensitites of the step features obtained with CO titration proved to be the most rigorous test of surface cleanliness, as impurity species are generally believed to segregate to step sites, blocking CO uptake at steps.

The mobilities of the adsorbed CO molecules on the (111) plane are manifested in the time-resolved data, examples of which are provided in Fig. 1. At low temperatures, such as $T=105$ K in Fig. 1(c), the CO are relatively immobile. The initial spectra exhibit a step-versus-spectral weighting that is representative of the statistical distribution of step and terrace adsorption sites. These data also verify that the initial adsorption is indeed spatially uniform. At higher temperatures, such as $T=144$ K in Fig. 1(b), the CO diffusion occurs significantly faster. The maximum time resolution of this experiment, 5 ms at 16-cm^{-1} resolution, just permitted an observation of CO mobility at $T=195$ K, shown in Fig. 1(a).

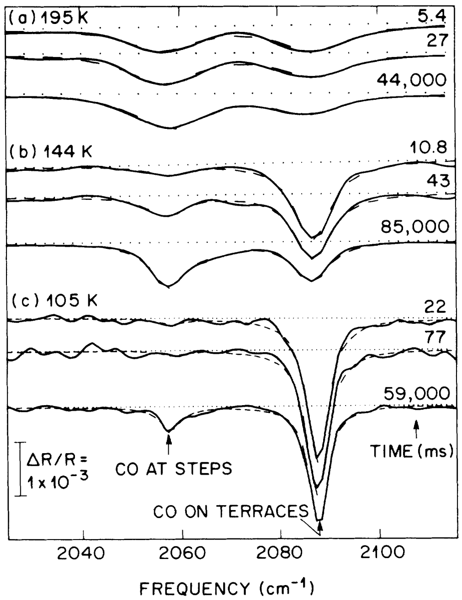

FIG. 1. A sampling of time-resolved spectra of CO/Pt[29(111)×1($\bar{1}$01)] for (a) $T=195$ K, $\theta_{CO}=0.005$ ML, and resolution $\Delta\tilde{\nu}=16$ cm^{-1}; (b) $T=144$ K, $\theta_{CO}=0.006$ ML, and $\Delta\tilde{\nu}=8$ cm^{-1}; (c) $T=105$ K, $\theta_{CO}=0.006$ ML, and $\Delta\tilde{\nu}=4$ cm^{-1}. Time, given in milliseconds (ms), is referenced to the arrival of CO molecules at the surface. Least-squares fits (dashed lines) employ a linear background (dotted lines) and Lorentzian functionals (Gaussian for the 16-cm^{-1}-resolution data) for the vibrational structures.

The infrared spectra were analyzed quantitatively through a least-squares fitting procedure, the results of which appear together with the linear backgrounds and unsmoothed data in Fig. 1. As pertinent to our quantitative analysis, we note that within our experimental accuracy in determining mode intensities ($>95\%$) no significant difference in mode intensity (or dynamical dipole moment) was observed between the carbonyl stretch of CO adsorbed at step sites and at terrace sites.

We have attempted to relate these observations to microscopic rate parameters through a simple kinetic model closely related to that of Serri, Tully, and Cardillo.[8] With the assumption of a single type each of step and terrace sites and perfect periodic symmetry of the surface, the system is equivalent to a one-dimensional lattice consisting of 28 terrace sites and one step site. The simulation determines the probability of occupation for each site at a given time. Site populations change if molecules are incident on the surface from the gas phase or if molecules already on the surface hop to or from the given site; desorption can be ignored at the experimental temperatures. For given temperature and coverage, three distinct hopping rates are employed: movement from a terrace site to one of its neighbors (T-T), from a terrace site to an adjacent step site (T-S), and from a step site to an adjacent terrace site (S-T). Only two of these rates are independent. Our primary interest is in the T-T rate since it represents diffusion on the perfect (111) plane. The T-S rate differs only in that we have assumed that some step sites are not accessible because they are blocked by molecules which have already diffused to the steps or by impurities at the steps. In the present model, each molecule adsorbed at a step blocks some number of consecutive step sites. From the equilibrium data we have determined this number to be approximately 8. The S-T rate has distinct microscopic rate parameters since the binding energy at step and terrace sites are different. Within transition-state theory, assuming that the transition state for each type of hop is identical implies that the difference in rates results from differences in the initial states. Thus the relative rates of S-T and T-T hops are determined from the equilibrium site populations, which are measured independently of the time-resolved data. By fitting the ratio of these rates with an Arrhenius form, we find that CO is more tightly bound at steps by about 8 kcal/mol (0.35 eV) and the prefactor for hopping from a step site is 10^2 times larger than from a terrace site. The 8-kcal/mol binding-energy difference is in agreement with thermal-desorption measurements on comparable surfaces.[9,10]

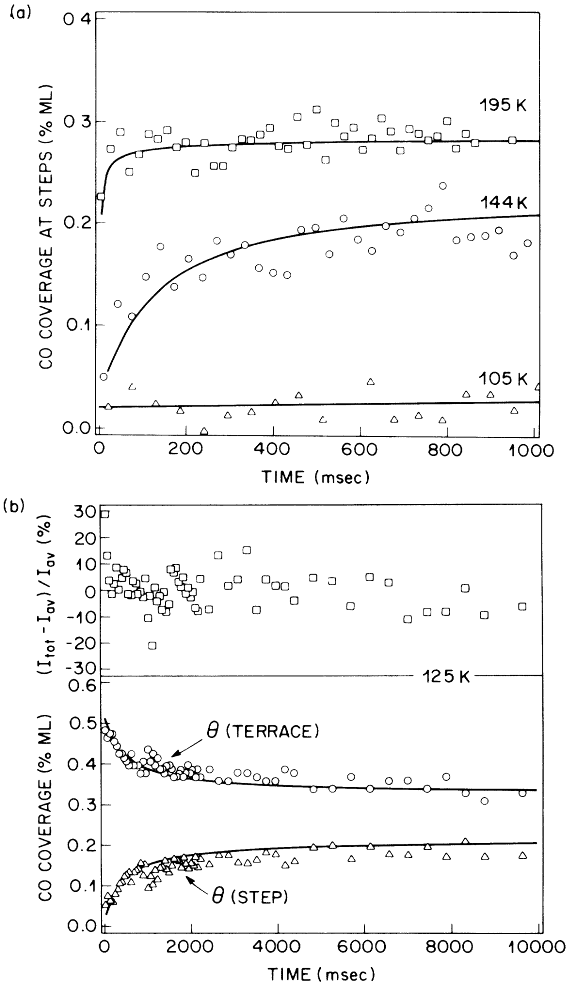

FIG. 2. (a) CO populations of the steps as functions of time for three different temperatures. The solid lines are simulations of the data, as described in the text, from which the terrace hopping rates are determined. (b) CO populations of terraces (circles) and steps (triangles) as functions of time for $T=125$ K shown together with the simulation (line). The corresponding percent fluctuations of the total measured infrared intensity, the squares appearing at the top of the figure, show a virtually constant value, indicating equal ir absorption by CO at steps and at terraces.

This leaves the T-T hopping rate as the only adjustable parameter to fit to the time-resolved data. For each temperature at which rate data are available, we have simulated the time dependence of step and terrace populations by using the experimentally determined values of total coverage and adjusting the terrace hopping rate to establish a good visual fit to the measured time dependence. Representative results are shown in Fig. 2. An Arrhenius plot of the rates over the entire range of temperatures follows in Fig. 3; the line represents a linear least-squares fit to the points shown. It determines the T-T hopping barrier to be 4.4 kcal/mol (0.19 eV) with a prefactor of 8×10^9 s^{-1}.

These values are considerably lower than the previous experimental findings.[11-13] These differences may be partially accounted for by considering the different experimental conditions: The field emission value of 14 kcal/mol was determined under high-field conditions and at higher coverage[11]; the laser-desorption value (7 kcal/mol) is extracted from macroscopic measurements of the diffusion constants and will be affected by micro-

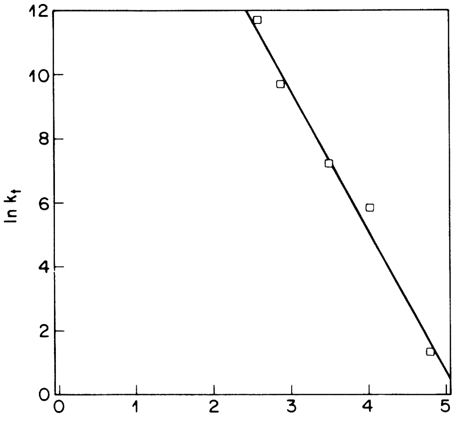

FIG. 3. Natural logarithm of the terrace hopping rate k_t as a function of inverse temperature. The solid line is a linear least-squares fit to the data yielding $\Delta E_t = 4.4$ kcal/mol (slope) and $A_t = 8\times10^9$ s^{-1} (intercept).

scopic surface defects.[12] Reporting a diffusion barrier of 7 kcal/mol, the helium-scattering determination[13] possesses the most similarities to the current study in that a microscopic rate of the filling of defect sites is measured.[14] Yet several differences in experiment and interpretation need be noted. As this previous work recorded diffusion to random defect sites, the observed rate of defect filling represents an average displacement. Poelsema, Verheij, and Comsa relied upon a simple model to determine an average diffusion rate, which neglects the details of defect filling and/or molecular interactions at defects. Under the conditions of their experiment, where the number of CO molecules is of the same order as the number of defect sites, we have found that the kinetics of defect filling is indeed affected by these interactions. Therefore we consider their value to be an upper bound to the diffusion barrier.

We acknowledge that the present experiment may be critically affected by (a) the degree of surface perfection (we assume an ideal step periodicity) and (b) our treatment of those kinetic processes occurring along the steps. We have noted that, at longer times, a third "step feature" becomes evident. We speculate that the long-time stability of this third feature is due to a one-dimensional ordering along the steps. Future investigations of crystals with higher step densities and different step morphologies should resolve these uncertainties.

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[14] From our measurement of microscopic hopping rates and a hopping length of 2.746 Å, corresponding to nearest-neighbor platinum distances, we can calculate macroscopic diffusion constants: $D_{(T=100\,\mathrm{K})} = 4.2\times10^{-16}$ cm^2/s and $D_{(T=195\,\mathrm{K})} = 2.5\times10^{-11}$ cm^2/s.