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Reaction of an H-atom beam with Cl/Au(111): Dynamics of concurrent Eley–Rideal and Langmuir–Hinshelwood mechanisms

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Studies of the reaction of H atoms with Cl chemisorbed on Au(111) reveal two dynamically distinct mechanisms. Some reactions occur on essentially a single gas-surface collision, by way of a so-called Eley-Rideal (ER) mechanism. Others occur between accommodated H and Cl atoms, by way of a so-called Langmuir-Hinschelwood (LH) mechanism. The dynamics of these processes has been characterized by combining molecular beam techniques with quantum-state-specific detection. Specifically, I have used molecular beam time-of-flight (TOF) techniques to determine angular and velocity distributions of the HCl product, and I have used resonance-enhanced multiphoton ionization to determine rotational and vibrational state distributions. The TOF and angular distributions provide clear evidence for the ER mechanism. This mechanism yields a fast (early) peak in the TOF distributions and a narrow angular distribution that is asymmetric with respect to the surface normal. Moreover, the peak in the angular distribution moves further away from the normal in the direction of the specular angle as the energy of the incident H atom is increased from 0.07 to 0.3 eV. The mean energy of the ER product is about 0.6 eV, but increases slightly with increasing incidence energy. In contrast, the LH mechanism yields a relatively slow (late) TOF component that approximately follows a Boltzmann distribution at the surface temperature (T_s) and disappears at $T_{\rm c} < 170$ K. The form of the angular distribution of this LH component is close to a cosine function. The fast (ER) TOF component is itself found to be composed of at least two contributions, assigned to HCl product formed in v=0 and v=1 (with some contribution from v=2). The rotational state distribution for the HCl(v=0) product of the ER mechanism is found to be distinctly non-Boltzmann, with a mean rotational energy of about 0.11 eV, or about 5% of the available energy. The rotational distributions obtained for v=1 and v=2 are similar to those for v=0. The relatively small fraction of energy channelled into rotation is a consequence of the low H-atom mass. In contrast, the rotational distributions for HCl(v=0) due to the LH mechanism are consistent with Boltzmann distributions at T_s . The vibrational state distribution for the ER process peaks in v = 1. The form of this distribution varies slightly with T_s , with about 30% in v = 0, 55% in v=1, and 15% in v=2 states at $T_s=600$ K. The mean vibrational energy for the ER component is thus about 0.32 eV, or $\sim 14\%$ of the available energy. This vibrational distribution is inconsistent with a simple attractive potential energy surface, which would lead to higher vibrational excitation. Either a large fraction of the energy is released as repulsion between the HCl and the surface, or vibrational energy is quenched, possibly by coupling between the departing molecule and the surface. The mean total energy carried away in the HCl product is only about half of that theoretically available. The total yield of the ER reaction increases rapidly with T_s , reaching a cross section of about 2×10^{-16} cm² per Cl atom at $T_s = 600$ K.

I. INTRODUCTION

Gas-surface reactions are generally classified in terms of two idealized mechanisms.¹ Most reactions are believed to occur between reagents that are chemisorbed and in thermal equilibrium with the surface, by way of a so-called Langmuir–Hinschelwood (LH) mechanism. Such reactions have been relatively well studied over the past decade or so. Certain highly facile reactions are thought to occur more or less directly as a gas-phase reagent strikes an adsorbate, by way of a so-called Eley–Rideal (ER) mechanism. In one limit, an ER mechanism could involve a single gas-surface collision. In fact, the incident reagent could "bounce" many times before reaction, being accommodated to varying degrees in the process.² Although these ideas have been discussed for more than 70 years, there have been relatively few experiments aimed specifically at probing gas-surface mechanisms in detail. This situation is rather surprising, since understanding the mechanisms of surface reactions is a basic requirement for modelling surface chemistry. A valid question in this context is the following: Do ER reactions ever occur? Accepting that they do, many dynamical questions arise. Do reactions occur on a single collision? How is the heat of reaction disposed? ER reactions should be far more exothermic than the LH counterparts, with an excess energy close to the heat of adsorption of the incident species. The fate of this excess energy will affect the entire energy balance of complex gas-surface systems. We should also like to see how closely ER reactions resemble gas-phase A + BC reactions (replacing C by the surface) since so much that already been learned about such systems.

Until recently, information on surface reactions came largely from kinetic measurements, relating the rate of reaction to the incident flux and to the surface coverage and

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temperature.¹ While such studies provide relatively convincing evidence for the case of the LH mechanism, evidence for the ER mechanism has been less than definitive. This evidence might involve, for example, observing that the reaction rate depends only weakly on surface temperature, or that the rate is proportional to the flux of incident reagents. While both observations are consistent with the ER picture, they fall short of proving that such a process occurs. Considering the importance of ER reactions (in interstellar chemistry, gaseous discharges, and catalytic processes, etc.), it is not surprising that a number of groups have sought to rectify this situation.

In order to prove that a reaction can occur on essentially a single gas-surface collision, dynamical measurements are required. The first such studies concerned the determination of internal state distributions of product molecules. Hall et al.³ and Los et al.⁴ found highly vibrationally excited hydrogen molecules issuing from cells in which H atoms are produced on a hot tungsten filament. Considering the energetics of the possible reactions, the excited molecules have been attributed to ER reactions between the incident atoms and those adsorbed on the metal walls of the cell. In one of these experiments, however, molecules were observed with more vibrational energy than should be available for an incident atom reacting with a chemisorbed atom even for a single collision,³ clouding the interpretation. Moreover, these studies involved poorly defined surfaces with poorly defined collection geometries. Lykke and Kay⁵ have carried out a more controlled study, involving the reaction of H atoms with Cl adsorbed on Au(111). These workers observed HCl in v=1with a rotational distribution that was essentially independent of T_s . The results again suggest an ER mechanism, but fall short of providing proof for such a process.

More recent dynamical studies have sought to probe ER reactions by looking for changes in the properties of the reaction product with changes in the energy of the incident species. Such measurements have recently been used to establish that atom abstraction can indeed occur by an ER mechanism. The first such study⁶ concerned the protonation of hyperthermal $N(C_2H_4)_3N$ molecules. Kuipers et al.⁶ showed that this molecule could pick up a proton from a Pt(111) surface, giving an ion whose translational energy depended on that of the incident molecule. More recently, Rettner⁷ studied the formation of HD from H atoms incident on D/Cu(111), and from D incident on H/Cu(111). The angular distribution of the HD was found to be asymmetrical about the surface normal. Moreover, this distribution was found to depend on the translational energy of the incident atom and on which isotope was incident.

These experiments have been complemented by a number of detailed computational studies. Elkowitz *et al.*⁸ and Tully⁹ have treated ER reactions classically. More recently, Kratzer and Brenig¹⁰ carried out model [two-dimensional (2D)] quantum calculations on the ER reaction of H atoms incident on H chemisorbed to W. They found that the H₂ product is formed in high vibrational states, in qualitative agreement with the experimental studies^{3,4} mentioned earlier. Jackson and Persson¹¹ obtained similar results from calculations for both W and Cu substrates. They concluded that the degree of vibrational excitation is sensitive to both the H/ metal binding energy and vibrational frequency. These workers also highlighted and rationalized the important differences between the possible isotopic combinations of H and D (H on D, D on D, etc.). Kratzer¹² has specifically addressed the experimental results for the H(D)+D(H)/Cu(111) system. One important conclusion from this work was that the observed angular distributions suggest that a fraction of the reactions proceeds by "indirect" events, where the incident atoms make several bounces in the surface well before reacting. In order to fully account for experimental findings for hydrogenic systems, however, higher dimensionality quantum calculations are probably needed.

The recent studies of ER reactions are also of considerable relevance to the interpretation of certain photochemical reactions. Such reactions are often initiated by the photolysis of a surface molecule,¹³ liberating a high-energy radical species. The dynamics of subsequent reactions may obviously be similar to those of ER reactions. For example, Mieher and Ho¹⁴ showed that CO and O₂ coadsorbed on Pt(111) yield CO₂ at 100 K when exposed to light with a wavelength below about 350 nm. These results suggest that O atoms formed in the photolysis of the O₂ react directly with the adsorbed CO. Measurements by Mullins *et al.*¹⁵ on the angular and velocity distributions of the CO₂ product of the reaction of a beam of O atoms with CO adsorbed on Pt(111) have since been shown to be consistent with those distributions from the photochemically induced reaction.¹⁶

In this paper, I report details of new measurements on the reaction of H atoms with Cl/Au(111).¹⁷ I have measured angular and velocity distributions of the HCl product using similar molecular beam scattering techniques to those used for the H+D/Cu(111) study. A brief account of this part of the study has appeared elsewhere.¹⁸ I have also repeated and extended the work of Lykke and Kay concerning the HCl internal state distributions. I confirm the proposal of Lykke and Kay⁵ that this reaction proceeds by way of both ER and LH mechanisms.

II. EXPERIMENT

The molecular beam apparatus employed in this study has been described in detail previously.¹⁹ Beams of H atoms are directed at a Au(111) single crystal saturated with atomic Cl. This sample is contained in an ultrahigh vacuum scattering chamber and mounted on a manipulator that provides accurate control of incidence angle, θ_i , and surface temperature, T_s . The crystal surface is cut to within 0.3° of the (111) plane. Surface contamination levels are below the 0.1% limit of Auger electron spectroscopy, except for oxygen, which is present at about the 1% level. This contamination is not decreased by sputtering. It is probably due to alumina imbedded in the soft metal surface during polishing. The surface is saturated with Cl₂ using a pulsed beam source that delivers several ML/s $[1 ML \sim 1.4 \times 10^{15} \text{ cm}^{-2} \text{ for Au}(111)]$. After heating the sample to 800 K, it is cooled to 400 K whereupon it is exposed to a 5 s dose, which is sufficient to achieve saturation. The sample is then heated or cooled to the required T_s . In some experiments, the surface was redosed at $T_s = 400$ K to resaturate the surface.

A. Beam sources

The measurements reported here are made using one of two different atomic beam sources. Relatively low energy $(\sim 0.07 \text{ eV})$ H-atom beams are generated using a microwave discharge source consisting of a quartz tube with a $\sim 2 \text{ mm}$ diameter hole.^{20,21} This source yields a beam that is about 80% dissociated and has an atomic flux of about 1 ML/s at the crystal position, which is $\simeq 30$ cm from the orifice. To obtain this high degree of dissociation, part of the hydrogen gas is bubbled through water, introducing $\sim 0.1\%$ water to the beam. No additional O is detected by Auger after exposure to this beam. The higher energy beams ($\sim 0.3 \text{ eV}$) are made by thermal dissociation in a graphite tube beam source operated at about 2200 K. Using a 2 mm diameter hole and a source pressure of a few Torr gives an atomic flux of about 0.2 ML/s, together with a molecular flux of \sim 5 ML/s (about 2% dissociation). H-atom beams from either source are chopped by a high-speed chopper, which reduces the flux by a factor of 200 and yields 6 μ s pulses for TOF measurements with a repetition rate of 800 pulses/s. For laser detection experiments, which are restricted to a 10 pulse/s repetition rate, beams are additionally modulated by a fast shutter. This shutter is constructed from a small solenoid (SP-37, Electro-Mechanisms, Inc.) that is synchronized to the chopper opening and to the firing of the laser. In this manner, the flux of H atoms to the surface is reduced by a further factor of 80. This measure prolongs the time required for the H-atom beam to remove Cl, and therefore allows longer time for acquisition of laser-ionization spectra. In the case of detection on the quadrupole mass spectrometer, there are no restrictions on the repetition rate, so this shutter is left open.

B. Angular and velocity distributions

Angular and velocity distributions are obtained using time-of-flight (TOF) techniques, similar to those described previously.¹⁹⁻²¹ Pulses of HCl product are detected at m/e=36 using a differentially pumped quadrupole mass spectrometer that can be rotated about an axis passing through and parallel to the crystal face. TOF distributions are referenced to the chopper opening. Zero time is determined optically by detecting light from the graphite source on a photomultiplier attached to a telescope looking down the beam axis. In order to obtain accurate information on the velocity of the HCl product, we must allow for the spread in arrival times of the incident H atoms. This distribution is determined by separate TOF measurements on the beams. The TOF analysis and convolution over the arrival times of the incident beam is similar to that described previously for energy transfer studies,¹⁹ except that in this system the velocity after the surface encounter is not related to the velocity of the incident species. Angular distributions are obtained by integrating the TOF signals for each angle. The mounting of the crystal is such that the scattering plane is close to the [101] azimuth, i.e., parallel to the atomic rows. The arrangement of Cl atoms relative to the Au atoms is not known with any certainty. Adsorption of Cl₂ gives a $(\sqrt{3} \times \sqrt{3})R30^\circ$ lowenergy electron diffraction (LEED) pattern,²² which is consistent with an adlayer structure that has rows of Cl along the [121] direction, with long bridges along the $[10\overline{1}]$ direction.²² The H-atom beam impinges on the surface at an incidence angle of 60° and the angular resolution is about 3°.

C. Internal state distributions

Quantum-state distributions are obtained by (2+1) multiphoton laser ionization of the HCl molecules via a twophoton resonance to either the $V^{1}\Sigma$ or $E^{1}\Sigma$ states, as described by others.^{5,23-25} Measurements are made on HCl(v=0) using the transitions to v'=11, 12, and 13 levels of the V state, which requires light at about 238 nm. This light is obtained from a Nd:YAG-pumped dye laser (Quanta-Ray, DCR2/PDL1) operated using SR690 dye (Exciton) diluted in methanol. The dye laser light is frequency doubled in KDP and mixed with residual 1064 nm radiation in a second KDP crystal. Measurements are made on HCl(v=1) and (v=2)using transitions to the v' = 0 level of the E state. The E - X(0,1) band is accessed using DCM dye (Exciton) diluted in methanol. The dye laser output is again doubled and mixed in KDP, giving light in the region of 247 nm. The E - X(0,2)band is accessed using Coumarin 500 dye (Exciton) in methanol. This dye laser output is doubled in BBO to give light in the region of 256 nm, giving about 3 mJ/pulse in a bandwidth ~ 0.5 cm⁻¹ [full width at half maximum (FWHM)], a pulse duration of 8 ns, and a repetition rate of 10 Hz. The laser beam is focused with a single plano-convex suprasil lens with a focal length of 260 mm to a point about 4 mm from the point where the molecular beam strikes the crystal. The crystal face is held parallel to the laser beam and rotated about an axis, giving an angular resolution of about 30° in the scattering plane with effective integration over all out-of-plane angles. For the experiments reported here, the crystal was held at an angle of 10° to the incident beam, rotated about the [101] azimuth. The laser beam passes through the chamber via two UHV suprasil windows (Insulator Seals), each of which transmit more than 90% of this radiation when clean.

III. RESULTS

A. TOF and angular distributions

TOF distributions have been obtained for the HCl product of the reaction of H atoms with the Cl/Au(111) surface for a wide range of conditions. These results have been analyzed to yield velocity and angular distributions. Specifically, I have measured TOF distributions for different detection angles, θ_f , for $T_s = 100$ and 300 K, using H-atom beams with mean energies of 0.07 and 0.3 eV. HCl is detected only upon exposing the Cl/Au(111) surface to an H-atom beam. Exposing the clean Au(111) surface to the beam yields no discernible features (at m/e=36) in the TOF distributions. Neither are signals observed when the Cl-saturated surface is exposed to an intense H₂ beam (e.g., with the microwave discharge turned off). Adding Cl₂ to the H-atom beam source chamber also fails to yield an HCl signal. The HCl signals are therefore attributed to the product of the reaction of H atoms with the chemisorbed chlorine. Cl₂ temperature programmed desorption (TPD) spectra are found to be very



FIG. 1. Time-of-flight distribution of HCl formed by the reaction of H atoms with Cl/Au(111). This distribution was obtained for $T_s = 300$ K at a detection angle of 33° from the surface normal. The incident H atoms have a mean kinetic energy of 0.07 eV and incidence angle of 60°.

similar to those reported previously,²² as are general trends concerning the sticking of Cl_2 to Au(111) as a function of T_s .

Most TOF distributions are obtained by collecting signal over a period sufficient for the H-atom beam to remove about half of the Cl coverage. Although signals decrease with decreasing Cl coverage, the form of the distributions are relatively insensitive to this coverage. The decrease in total product signal with increasing exposure to the H-atom beam is approximately linear for $T_s = 300$ K. At $T_s = 100$ K, the decrease is approximately exponential with increasing exposure [plots of ln(signal) vs time are linear]. The rate of removal at $T_s = 600$ K is consistent with a reaction probability of unity, within experimental uncertainties of about a factor of 2. After an exposure sufficient to reduce the signal to about 25% of maximum at $T_s = 100$ K, warming the surface to 300 K, then cooling again to 100 K, causes the signal to drop to essentially zero. This observation indicates that H atoms present on the surface at 100 K react and remove Cl as the surface is warmed.

TOF distributions of the HCl product are bimodal in many cases, as is evident from Fig. 1. This distribution was obtained for $T_s = 300$ K, with a detection angle of $\theta_f = 33^\circ$ with respect to the surface normal. The two components have approximately equal peak intensities under these conditions. The ratio of the two components changes significantly with θ_f , however, indicating that the two channels have different angular distributions. Figure 2 displays results obtained under similar conditions, but with $\theta_f = 0^\circ$, 30°, and 45°. The form of the later peak changes with T_s . Moreover, this feature disappears from TOF spectra for $T_s < 170$ K, as is apparent from Fig. 3, which compares TOF distributions for T_s =400 and 100 K for θ_f =0°. (The signals persist, however, down to $T_s = 140$ K, contributing to the TOF background, since they become too spread out in time to yield a TOF peak for $T_s < 170$ K.) The absolute intensity of the fast peak is similar in both cases.

The threshold temperature, below which the slow component disappears, corresponds closely to the temperature at which HCl desorbs from the Cl-saturated surface. TPD spectra of HCl (obtained with a heating rate of ~ 3 K/s) display a threshold of about 140 K, have a peak at about 165 K, and



FIG. 2. Time-of-flight distributions of HCl formed by the reaction of H atoms with Cl/Au(111). Results are displayed for $T_s = 300$ K for detection angles of 0°, 30°, and 45° with respect to the surface normal. The incident H atoms have a mean kinetic energy of 0.07 eV and incidence angle of 60°. The curves indicate the results of fits to the data. The energy axis along the top of the figure is only approximate. Accurate energies are obtained by the fitting procedure described in the text. The mean kinetic energy of the fast components is about 0.6, 0.5, and 0.25 eV, for $\theta_f = 0^\circ$, 30°, and 45°, respectively. The fits to the $\theta_f = 0^\circ$ data yield $T_{eff} = 330$ K for the slow component and $u_0 = 860$ m/s and $\alpha = 900$ m/s for the fast component. For $\theta_f = 30^\circ$, I obtain $T_{eff} = 285$ K, $u_0 = 700$ m/s, and $\alpha = 550$ m/s.

tail off to zero by $T_s=210$ K. Exposing the Cl-covered surface to H atoms yields the same HCl TPD spectrum as for directly adsorbing a beam of HCl on the Cl-covered surface. The adsorption probability of HCl on this surface is quite small, however, of the order of 0.01 (HCl does not remain adsorbed on the bare surface at 100 K).

The TOF distributions can be analyzed to obtain information on the velocity distributions of the HCl product. The analysis is similar to that employed previously for inelastic scattering studies.^{7,19,26} Most distributions can be accounted for by assuming that they are composed of two separate contributions from products with different velocity distributions. The TOF analysis indicates that the broad temperaturedependent feature is approximately described by a Maxwell– Boltzmann distribution of velocities. In contrast, the feature at early times is found to have a relatively narrow velocity distribution, with a mean energy far in excess of kT_s . Specifically, the slow components correspond to velocity distributions of the form:

$$f(u) \propto u^3 \exp(-mu^2/2kT_{\text{eff}}), \qquad (1a)$$

while the fast components are fitted to the form:

$$f(u) \propto u^3 \exp[-(u-u_0)^2/\alpha^2].$$
 (1b)





FIG. 3. Time-of-flight distributions of HCl formed by the reaction of H atoms with Cl/Au(111). Results are displayed for T_s =400 and 100 K for θ_f =0°. The incident H atoms have a mean kinetic energy of 0.07 eV and incidence angle of 60°. The curves indicate the results of fits to the data, as discussed in the text. The energy axis is again approximate. The mean kinetic energy of the fast components in about 0.6 eV.

No allowance is made for any residence time prior to reaction. The curves added to Figs. 2 and 3 correspond to such fits.

1. Fast TOF component

(a) Angular distributions. Angular distributions have been obtained by integrating the TOF signals for beam energies of 0.07 and 0.3 eV, and for $T_s = 100$ and 300 K. The results for $T_x = 100$ K are displayed in Fig. 4 in polar form. The curves added to the data are provided as a guide to the eye. These results correspond to the relative signals at each angle. They have not been corrected for the 1/u sensitivity of the detector. These angular distributions are asymmetric about the surface normal. Although the deviations are small, they are much larger than the experimental uncertainties. Angles are calibrated to about 0.1° using He-atom scattering immediately after experiments. Increasing T_s is associated with a slight broadening in the angular distribution. Figure 5 displays a comparison of results for $E_i = 0.07$ eV with $T_s = 100$ and 300 K. The 100 K results are the same as in Fig. 4.

(b) Velocity distributions. Analysis of the fast component of the TOF distributions yields a mean energy of between 0.5 and 0.8 eV, depending on E_i , θ_f , and T_s . The most detailed studies have been carried out at $T_s=100$ K using a beam with $E_i=0.3$ eV. Low T_s ensures that the slow component is absent, and the higher energy beam provides better TOF resolution. Under these conditions, the TOF's of the fast components are themselves found to composed of more than one component. Attempts to fit the distributions to a single component are generally unsatisfactory. This behav-



FIG. 4. Polar plot of the angular distributions of the HCl product of the reaction of H atoms with Cl/Au(111) for $T_s = 100$ K (signal intensities are proportional to the distance from the origin). Results are displayed for incidence energies of 0.07 and 0.3 eV, as labeled. The angle of the incidence beam (60°) is indicated graphically by the arrow. These results are attributed to an ER mechanism. The broken line corresponds to $\cos \theta_f$, which is expected in the absence of dynamical factors. The tics are placed at 10° intervals.

ior is illustrated in Fig. 6, which displays a TOF distribution obtained for $\theta_f = +25^\circ$ (positive angles are specular side of the normal). The upper panel of Fig. 6 shows a best fit to a single component model, of the form of Eq. (1b). It is apparent that the fitted curve only approximately follows the observed form. The lower panel in Fig. 6 shows a fit to a model in which the distribution is considered to be the sum of two components (referred to a components x and y) of the form of Eq. (1b); this fit requires six parameters. Two parameters are required to describe the form of each of two components;



FIG. 5. Effect of surface temperature on the angular distribution of the HCl product of the reaction of H atoms with Cl/Au(111). Results are displayed for T_s =100 K (solid curve) and T_s =300 K (broken curve), both for E_i =0.07 eV. The 100 K results are the same as in Fig. 4.





FIG. 6. HCl TOF distribution obtained at $\theta_f = +25^\circ$ for $E_i = 0.3 \text{ eV}$ and $T_s = 100 \text{ K}$. This distribution cannot be satisfactorily fit with a single component model, of the form of Eq. (1b). The upper panel shows a best fit to such a single-component model. The lower panel shows a fit to a model in which the distribution is considered to be the sum of two components of the form of Eq. (1b).

 $v_0(x)$ and $\alpha(x)$ for one, and $v_0(y)$ and $\alpha(y)$ for the other. One additional parameter is required to control the fraction of each component, plus one final parameter for the overall normalization.

I have fitted TOF distributions obtained at different angles in a number of ways. As a starting point, all six parameters were allowed to vary in the fits. In other cases some of the parameters were held constant in order to reduce the number of parameters needed to describe the data. Inspection of the results indicates that a satisfactory set of fits can be

FIG. 7. HCl TOF distributions obtained for $E_i=0.3$ eV and $T_s=100$ K for $\theta_f=+15^\circ$, 0°, and -15° , as labeled. The curves correspond to fitted curves assuming that each distribution is composed of two components.

obtained using $\alpha(x)$ and $\alpha(y)$ values of 500 and 600 m/s, respectively, for the faster and slower of the two components. The $u_0(x)$ values are then found to be about 2000 m/s and the $u_0(y)$ values are found to be between 400 and 1300 m/s. Table I lists a set of results obtained from fits to TOF distributions for E_i =0.3 eV and T_s =100 K.

The relative contributions of the two components is found to vary systematically with final angle. This point is illustrated in Fig. 7, which shows TOF distributions for $\theta_f = +15^\circ$, 0°, and -15° , together with their corresponding fitted curves (positive angles are on the specular side of the normal, negative on the opposite side). Here it is seen that the contribution of component x is largest for $\theta_f = -15^\circ$ and is very small for $\theta_f = 0^\circ$. Figure 8(c) displays values of the

θ_f (deg)	E_f (eV)	F_x^{a}	$u_0(x)$ (m/s)	E_x (eV)	u ₀ (y) (m/s)	E_{y} (eV)
-25	0.70	0.84	1840	0.79	490	0.23
-20	0.76	0.85	1900	0.84	680	0.28
-15	0.74	0.75	1950	0.87	860	0.35
-10	0.68	0.49	2020	0.92	1120	0.45
-5	0.61	0.27	2080	0.97	1180	0.48
0	0.58	0.07	2090	0.98	1220	0.50
5	0.58	0.09	2100	0.98	1240	0.51
8	0.58	0.12	2080	0.97	1250	0.51
10	0.62	0.26	2090	0.98	1230	0.50
15	0.67	0.48	2000	0.91	1120	0.45
20	0.71	0.62	2000	0.91	1010	0.40
25	0.72	0.71	1940	0.86	880	0.35
30	0.62	0.65	1850	0.79	750	0.31
35	0.53	0.63	1690	0.69	610	0.26
40	0.46	0.52	1670	0.68	440	0.21
50	0.38	0.71	1310	0.48	10	0.14
60	0.21	0.13	1380	0.51	170	0.16

TABLE I. Summary TOF fit parameters for $E_i = 0.3$ eV, $T_s = 100$ K [$\alpha(x)$ and $\alpha(y)$ constrained to 500 and 600 m/s, respectively].

^aFraction of component x used in fit (flux weighted).

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FIG. 8. Angular dependence of the HCl product of the reaction of H atoms with Cl/Au(111) for $E_i=0.3$ eV and $T_s=100$ K. (a) Angular distribution of total signal. (b) Mean energy derived from TOF analysis. (c) Fraction of component x obtained from analysis of the TOF distributions assuming a two component fit, as described in the text.

fraction of component x as a function of θ_f . The plotted fractions were obtained from fits in which the two α values were held fixed at $\alpha(x)=500$ m/s, and $\alpha(y)=600$ m/s. While different choices of these parameters, or a free fit to all the parameters, give quantitatively different results, the same qualitative trends are found. This trend can be understood by careful examination of Fig. 7, from which it is apparent that the distribution for $\theta_f \sim 0^\circ$ is lacking the fast leading edge that requires component a. These results indicate that the angular distribution of the component x has a minimum close to the surface normal. If the out-of-plane distribution resembles the in-plane distribution, the angular distribution for component x will be a "doughnut" or ring, with a depression in the middle.

This angular variation in the TOF distributions is reflected in the mean final energy of HCl product obtained under these conditions. Figure 8(b) shows the dependence of this mean energy on θ_f . Notice how the mean final energy falls rapidly with increasing θ_f beyond $\theta_f=25^\circ$. This trend is correlated with a drop in the fraction of component *a*. Averaging the final energy over angle yields an overall mean final energy of 0.61±0.05 eV. The limited measurements made with $E_i=0.07$ eV yielded a significantly lower final energy than for $E_i=0.3$ eV. At $\theta_f=0^\circ$ and $T_s=100$ K, decreasing E_i from 0.3 to 0.07 eV causes the mean energy of the HCl product to fall from 0.56 to 0.50 eV (although the absolute uncertainties may be as large as ±0.05 eV, the relative uncertainties are much smaller).

2. Slow TOF component

(a) Angular distributions. Angular distributions have also been obtained for the slow component of the TOF's obtained at $T_s = 300$ K. The signal at a given angle is determined by fitting the TOF distribution to a bimodal form, as



FIG. 9. Angular distribution of the slow component of the HCl product of the reaction of H atoms with Cl/Au(111) for E_i =0.07 eV and T_s =300 K. The solid line is cosine raised to the power of 1.4.

in Fig. 2, then integrating the distribution over the slow component only. Again, the relative intensities have not been corrected for (the small) differences in final velocities and so represent density, rather than flux, distributions. Figure 9 shows the resulting angular distribution.

(b) Velocity distributions. Analyzing TOF distributions for different θ_f at T_s =300 K, the effective temperature of the slow component is found to decrease slightly with increasing θ_f , from values slightly over the surface temperature for θ_f =0°, to less than 250 K for θ_f >70°. This behavior is illustrated in Fig. 10, which displays T_{eff} vs θ_f for T_s =300 K. The slight cooling in T_{eff} with θ_f is relatively independent of fitting method. For example, an analysis in which the fast component is ignored and the TOF is simply fit to a Boltzmann gives similar results to the full analysis, provided that the fit is restricted to the slow part of the distribution, where the fast component would not be expected to contribute.



FIG. 10. Angular variation of the effective translational temperature of the slow component of the HCl product of the reaction of H atoms with Cl/Au(111). Results are for $E_i=0.07$ eV and $T_s=300$ K. The corresponding signal intensities are displayed in Fig. 9.



FIG. 11. Multiphoton laser ionization spectra of HCl(v=0) molecules obtained via a two-photon resonance to the $V^{1}\Sigma$ state, using the (13-0), (12-0), and (11-0) bands, as indicated. (a) Spectrum for an effusive HCl beam for a nozzle temperature of 1850 K. (b) Spectrum for the HCl product of the reaction of H atoms with Cl/Au(111), for $E_i=0.07$ eV and $T_s=100$ K. The lines marked with an asterisk are due to ionization of Cl. (c) Spectrum obtained under the same conditions as (b) but with $T_s=273$ K.

B. Internal-state distributions

The aforementioned studies of the angular and velocity distributions of the HCl product have been complemented by measurements of quantum-state distributions. Specifically, I have obtained the vibrational state distribution for the HCl product as a function of surface temperature, and I have determined the rotational state distributions for each of the v=0, 1, and 2 states. These results also reveal two dynamically distinct reaction mechanisms, one of which yields molecules that are approximately accommodated to T_s , the other of which yields a highly excited product. As for the angular and velocity measurements, the accommodated component is found to disappear at low T_s . Since these signals are not resolved in time, they disappear at a lower temperature than for the TOF measurements, at $T_s < 140$ K. All results were obtained using an incidence angle of 10°. The results correspond to averages over the entire velocity distribution of the product molecules, since the laser is focused only a few millimeters from the surface. Moreover, the laser detection has an angular resolution of about 30° (FWHM) in the scattering plane, with effective integration over all out-of-plane angles.

1. HCI(v=0) product

HCl(v=0) is a product of both reaction mechanisms. Figure 11 shows spectral scans for the detection of HCl in



FIG. 12. Boltzmann plots of the rotational distributions of HCl(v=0) formed by the reaction of H atoms with Cl/Au(111). Results are displayed for surface temperatures of 273 and 100 K. The measurements at these two temperatures are scaled accurately with respect to each other, indicating that much larger signals are obtained at the higher temperature. The line on the 273 K results is a fit to the data, yielding a rotational temperature of 350 K. A similar linear fit to the 100 K data yields a rotational temperature of 1400 K. This data is clearly do not fall on a straight line, however. The lines shown on the $T_s=100$ K data are provided as a guide to the eye. The incident H atoms have a mean kinetic energy of 0.07 eV and incidence angle of 10°.

the ground vibrational state using (2+1) resonance-enhanced multiphoton ionization detection.^{5,23-25} The lowest panel shows the spectrum obtained upon exposing the Cl/Au(111) surface to the H-atom beam at a surface temperature of 273 K. The resulting spectrum is characteristic of molecules accommodated to T_s , and is, in fact, very similar to that obtained from background HCl admitted to the chamber through a leak valve. In this latter case, the effective rotational temperature is found to be $\sim 300 \pm 20$ K. The middle panel of Fig. 11 shows a spectrum obtained upon exposing the Cl/Au(111) surface to the H-atom beam at a surface temperature of 100 K, where the accommodated component is absent. Although the overall intensities are smaller, many more lines are apparent. Rotational states up to J=15 are readily identified. In this case the populations do not quite follow a linear Boltzmann plot, as can be seen from Fig. 12. Figure 12 displays plots of $\ln\{N_I(2J+1)\}\$ vs the rotational energy, E_R , for $T_s = 273$ and 100 K. A Boltzmann distribution would yield a straight line on such a plot, with a slope proportional to the rotational temperature. The approximate rotational temperatures are 350 and 1400 K, respectively. The mean rotational energy at $T_s = 100$ K is about 0.11 eV. The two plots in Fig. 12 are accurately scaled to each other (using the T_s dependence of specific lines). The signal obtained at $T_s = 273$ K is therefore much greater than for $T_s = 100$ K at low J. At high J the differences are smaller. The contribution to J=10 approximately doubles upon rais-



FIG. 13. Boltzmann plots of the rotational distributions of HCl(v=0) formed by the reaction of H atoms with Cl/Au(111). Results are displayed for surface temperatures of 273 and 600 K. The broken lines indicate the slopes expected for $T_r = T_s$. We attribute the excess population at high J to an ER mechanism. The measurements at these two temperatures are scaled accurately with respect to each other. The incident H atoms have a mean kinetic energy of 0.07 eV and incidence angle of 10°.

ing T_s from 100 to 273 K. Further increasing T_s causes an increase in T_r , but has only a weak effect on overall signal intensities. This behavior is illustrated in Fig. 13, which shows results for $T_s=273$ K compared to results for $T_s=600$ K. Results are again accurately scaled. The results for $T_s=600$ K yield $T_r=840$ K. Further investigation of the T_s dependence of v=0 signals reveals that the ratios of populations at high J (J>12) are insensitive to T_s . The results for $T_s=273$ and 600 K are thus found to be consistent with rotational distributions formed from the sum of a Boltzmann distribution with $T_r=T_s$ plus a fixed distribution equal to that obtained at $T_s=100$ K. The amount of this fixed distribution increases with increasing T_s . (I will argue later that the Boltzmann component is due to an LH mechanism, and the fixed component is due to an ER mechanism.)

Signals are also observed from laser ionization of atomic Cl. The line positions are consistent with those reported by Arepalli *et al.*²⁷ These lines are indicated by an asterisk in Fig. 11. Lykke and Kay⁵ reported observing Cl atoms in this system under very similar conditions. I also observe a number of other lines that I am unable to identify. The upper panel in Fig. 11 shows the spectrum obtained from a beam of HCl issuing from the graphite nozzle at a temperature of 1850 K. It is seen that this spectrum is quite similar to that of the product for $T_s = 100$ K, but it is clear that there are fewer lines.

2. HCl(v=1) product

A large fraction of the reaction product is found to be in the v = 1 state. A spectrum of the E - X (0,1) band recorded for the HCl product with $T_s = 600$ K is shown in Fig. 14. Initial analysis of such spectra yielded a relatively cold rotational distribution, consistent with a T_r of about 380 K. This



FIG. 14. Spectrum of the HCl E-X (0,1) band for the HCl product of the reaction of H atoms with Cl adsorbed on Au(111) with $T_s=600$ K. Conditions are the same as for Fig. 11. This spectrum is very similar to that reported by Lykke and Kay (Ref. 5).

rotational temperature was found to be essentially independent of T_s . These results are in good qualitatively agreement with the observations of Lykke and Kay⁵ who reported that the rotational temperature of the HCl(v=1) product is 300 ± 50 K for $T_s=300$ to 700 K. I have found, however, that the line strength factors for the Q-branch transitions of the E-X (0,1) band system (employed both by us and by Lykke and Kay⁵) decrease rapidly with increasing J. Correcting the observed line intensities for these decreasing line strengths brings the distributions into good agreement with those for the v=0 product.

The relative line strengths are obtained by measuring rotational distributions for beams of HCl, using nozzle temperatures up to 2000 K. Both the (0,0) and (0,1) bands of the E-X system yield much colder rotational distributions than for the (13,0), (12,0), and (10,0) bands of the V-X system. The line strengths of the Q branch transitions for J>4 are reduced because of perturbations to the E - X v = 0 level. The relative line strength factors are close to unity for Q(0)to Q(4), then fall to 0.95, 0.73, 0.40, 0.20, and 0.10 for Q(5) to Q(0), respectively. I have not been able to assign unambiguously Q(10) transitions and higher. Similar detection anomalies have been reported by Spiglanin et al.²¹ for the HCl E - X (0,0) band. They found even smaller relative effective line strength factors of 0.71 for Q(5), 0.43 for Q(6), and 0.23 for Q(7). I believe that the difference can be attributed to the different laser power employed in the two studies. If the reduced ionization efficiency is due to competition with a quenching process (e.g., rotational predissociation) then the relative detection efficiency for high J vs low J



FIG. 15. Boltzmann plots of the rotational distributions of HCl(v=1) formed by the reaction of H atoms with Cl/Au(111). Results are displayed for surface temperatures of 100 and 600 K. The open symbols show the relative signals obtained without correcting for decreasing line strengths for Q(5) and above. The dashed lines are fits to these data, yielding apparent rotational temperatures of 500 and 380 K for $T_s = 600$ and 100 K, respectively. The solid symbols show results corrected for the line strength factors given in the text. The curved lines are obtained from a quadratic fit to the v = 0 distribution displayed in Fig. 12 for $T_s = 100$ K. The measurements at 100 and 600 K temperatures are scaled accurately with respect to each other, indicating that much larger signals are obtained at the higher temperature. The incident H atoms have a mean kinetic energy of 0.07 eV and incidence angle of 10°.

will increase as the ionization rate is raised with increasing laser power. Spiglanin *et al.*²¹ used only 150 μ J/pulse, compared to about 3 mJ/pulse in the present study. Lykke and Kay⁵ used 5 mJ/pulse, but used a lens with a slightly longer focal length (35 cm compared to out 26 cm).

Figure 15 displays Boltzmann plots for $T_s = 600$ and 100 K. As for the v=0 data, the results for different T_s are accurately normalized. The open symbols in Fig. 15 indicate the populations obtained without allowing for the decreasing line strengths. These results yield apparent rotational temperatures of 500 and 380 K, for T_s =600 and 100 K, respectively. The solid symbols in Fig. 15 indicate the corrected results, using the relative line strength given earlier. The small differences in apparent effective rotational temperature (deduced without correcting for line strengths) between the two surface temperatures, and between this work and the work of Lykke and Kay,⁵ are not significant, considering that the line strength factors actually vary somewhat with laser power. The curved lines are obtained from a quadratic fit to the rotational distribution for v = 0 for $T_s = 100$ K. I consider the rotational distributions for v=0 and v=1 to be indistinguishable over the limited range of J's measured for v = 1.

In separate experiments, the rotational distribution was also obtained for HCl(v=1) using the high temperature beam source, with $E_i \sim 0.3$ eV. The resulting distribution was indistinguishable from that obtained with the microwave



FIG. 16. Spectrum of the HCl E-X (0,2) band for the HCl product of the reaction of H atoms with Cl adsorbed on Au(111) with T_s =600 K. Conditions are the same as for Fig. 11.

source, $E_i < 0.1$ eV. I conclude that the distribution for molecules with J=0-8 is insensitive to E_i .

3. HCl(v=2) product

I have also detected HCl in the v = 2 state. A spectrum of the E-X (0,2) band recorded for the HCl product with $T_s = 600$ K is shown in Fig. 16. From the similarity of this spectrum to that for the (0,1) band, I conclude that the rotational state distribution for molecules in v=2 is similar to those for v = 0 and 1. As in the case of the E - X(0,1) band, I believe that the intensities of the high J lines are anomalously low because of a falloff in the line strength factors for J>5. The high J's have slightly higher intensities than for the (0,1) band because of the higher power and different focusing geometry employed for the (0,2) band. [Light in the region of the (0,2) band is obtained by doubling the frequency of a dye laser operated using a Coumarin dye. The low gain of this dye requires a different dye laser configuration, which results in a different beam divergence. Since there is no need to shift the frequency of the doubled light in a second nonlinear crystal, higher powers are obtained.]

4. Vibrational state distributions

In order to assess the fraction of molecules leaving the surface in each vibrational state, the detection efficiency has been calibrated for v=1 compared to that for v=0 and for v=2 compared to v=1. Specifically, I detected HCl from a graphite nozzle at 1900 K. Using a nearly effusive beam (Mach number ~ 1) I measured relative signals for laser detection using the V-X (11-0) and E-X (0-1) bands, for



FIG. 17. Dependence of the HCl signals on surface temperature for molecules in the v=0, v=1, and v=2 states (dots, squares, and triangles, respectively). (a) Results for J=3 of each state. The dashed curve indicates the contribution to the v=0 signal due to an ER mechanism. (b) Results summed over the rotational distributions. The dashed curve indicates the contribution to the v=0 signal due to an LH mechanism. The lines are provided as a guide to the eye.

detecting molecules in v=0 and v=1, respectively. Assuming no vibrational relaxation in the expansion, I calculate that the sensitivity to v=1 is 0.7 ± 0.2 of that for detecting v=0, using the same laser power and very similar focusing conditions for each band. With this information, I am able to compare directly v=0 and v=1 product intensities. At $T_s=100$ K, the signal for v=1, J=3 is about 60% of that for v=0, J=3. Allowing for the 70% detection efficiency, the intensity from these two states is the same within the uncertainties at this surface temperature. For $T_s > 140$ K, where the accommodated component contributes, the v=0 signals exceed those for v=1 for T_s up about 600 K. At $T_s=700$ K, the v = 1 signals are slightly larger than those for v = 0. The relative v=0 and v=1 intensities are displayed in Fig. 17 as a function of T_s . The rapid rise in the v=0 signal around 150 K corresponds to the onset of the HCl desorption from the Cl-covered surface. Notice that the approximate equality of v=1 and v=0 products at $T_s=100$ K apparent in Fig. 17 is consistent with estimates based on the TOF measurements. Inspection of Fig. 8 indicates that the fraction of component a of the TOF distributions averaged over the angular distribution is indeed approximately 0.5 at this T_s .

As mentioned in Sec. III B 1, the rotational distributions for v = 0 at high T_s can be accounted for assuming that they result from the sum of a distribution with $T_r = T_s$ together with a distribution of the form obtained at $T_s = 100$ K (sum of LH and ER components). The contribution due to the fixed (ER) distribution can be deduced from the intensities of the high-J lines, which would barely be detectable for a distribution with $T_r = T_s$. If we assume that the form of this fixed contribution is indeed independent of T_s , we can separate



FIG. 18. Vibrational state distribution for the HCl product of the reaction of H atoms with Cl adsorbed on Au(111). The solid bars indicate the distribution for the ER mechanism. The shaded region indicates the additional contribution to v = 0 due to the LH mechanism, summing over all J. The dashed line indicates the contribution that would be obtained for J=3.

the v=0 signal into LH and ER components. The broken line in the upper panel of Fig. 17 shows the contribution of the ER or fixed component to the total J=3, v=0 signal. The lower panel of Fig. 17 shows the relative product yield for each vibrational state summed over J, assuming that the rotational distribution of the ER component is independent of vand that the rotational distribution of the LH component is given by a Boltzmann distribution at T_s . This correction substantially reduces the relative contribution from the LH component.

Signals for the E - X (0,1) and (0,2) bands have been compared in separate experiments for the same nearly effusive HCl beam. In this case, the power for the (0,1) band was 1.6 mJ, while that for the (0,2) band was 2.6 mJ. Even so, the sensitivity to v=2 is found to be only about 0.5 of that for v = 1. This low sensitivity could be related to the fact that the three-photon energy at 256 nm is getting close to the ionization potential (12.7 eV). Measurements on the HCl product performed with these same laser intensities indicate that the population of the HCl(v=2, J=1-4) product is about 0.25 of that of the HCl(v=1, J=1-4) product for $T_s=600$ K. The full temperature dependence of the v=2 contribution is given in Fig. 17. Figure 18 shows a vibrational state distribution for $T_s = 600$ K. The solid bars correspond to the ER component. The mean vibrational energy for the ER component is thus about 0.32 eV, or $\sim 14\%$ of the available energy. The shaded component of the v=0 bar indicates the relative signal for the LH component summed over J. The open part of the bar indicates the relative contribution observed for J=3 alone. (Recall that the rotational distribution for the LH component is colder, with a higher fraction of population in low J states compared to the ER component.)

It is apparent from Fig. 17 that both the v=1 and v=2 signals increase steadily with increasing T_s , as does the ER



FIG. 19. Plot of the logarithm of the HCl signals vs $1/T_s$ for molecules in v=0, v=1, and v=2 vibrational states (dots, squares, and triangles, respectively). The solid line indicates an activation energy of 550 cm⁻¹ (790 K), reported by Lykke and Kay (Ref. 5).

contribution to the v=0 signal. Figure 19 shows the results plotted on a logarithmic scale against $1/T_s$. We see that the signals increase approximately exponentially above $T_s=273$ K. The broken line corresponds to a slope of 550 cm⁻¹, as reported by Lykke and Kay,⁵ for the v=1 signal with T_s in the range 300 to 700 K. The v=0 signals increase slightly less rapidly than the v=1 signal, while the v=2 signals increase slightly more rapidly.

C. Reaction cross sections

Comparing the rate of removal of Cl with the incident H-atom flux, I estimate that the total probability for Cl removal is >0.5 at 600 K for the saturated surface. The J-integrated LH signal shown in Fig. 17(b) is seen to fall slightly with increasing T_s . Since I believe that the velocity of this component increases with increasing T_s , the LH flux is approximately constant for $T_s > 300$ K. (Laser ionization signals are proportional to density. Flux is proportional to density times velocity.) Yet the ER signals clearly increase with increasing T_s . The removal cross section must thus continue to rise with increasing T_s . From these observations, I conclude that the probability of Cl atom removal through the ER mechanism must be somewhat less than 1, even at the highest T_s . The cross section for Cl removal must be ~0.7 ± 0.2 times the area occupied by each Cl atom. Taking the Cl radius to be 1.2 Å on the saturated surface²² gives a cross section for Cl removal at about 600 K of $\sim 3 \pm 1 \times 10^{-16}$ cm², per Cl atom.

From Fig. 17(b) we see that the signal due to the ER mechanism is about 6 times greater than that from the LH mechanism at 600 K. The laser experiments do not necessarily integrate over all angles, however, so the relative contri-

bution from the LH mechanism could be higher. In fact, Figs. 5 and 9 indicate that the angular distribution of the accommodated component is twice as wide as the direct component at $T_s = 300$ K. Figure 2 shows that the two components are approximately equal at the normal. So from TOF measurements, I estimate that the angle-integrated signal from the accommodated component is up to 4 times that of the direct component at 300 K. From Fig. 17 I deduce only a factor of 2. Thus the LH signals obtained in the laser experiments may be a factor of 2 smaller than if we were truly to integrate over all angles. But this factor is coincidentally close to another correction factor that acts in the opposite direction. The velocities of the ER products exceed those for the LH product by about a factor 2, which means that the ratio of ER to LH fluxes are twice as high as is indicated by Fig. 17. I conclude that measurements of the angle-integrated fluxes of the LH and ER mechanisms would roughly follow Fig. 17(b). Approximate cross sections for the different processes can thus be obtained by multiplying the relative probabilities of Fig. 17(b) by 1.5×10^{-16} cm² per Cl atom.

IV. DISCUSSION

The TOF and angular distributions indicate that HCl is formed in this reaction by both ER and LH mechanisms. These conclusions are supported by the measurements of the internal-state distributions. I attribute the fast and slow components of the TOF distributions to ER and LH mechanisms, respectively. These two mechanisms are considered in turn.

A. Eley–Rideal dynamics

1. General considerations

Several of the results essentially prove that HCl is formed in part by an ER mechanism in this system. The strongest evidence comes from the angular distributions. The sensitivity of the angular distributions of the fast TOF component to the energy of the incident H atom (Fig. 4) can only be understood in terms of a direct gas-surface reaction. Similarly, the fact that these distributions are asymmetric with respect to the surface normal demands a direct ER-type mechanism, as does the fact that the shapes of the TOF distributions are different for equal detection angles on either side of the normal (Figs. 7 and 8). The absence of symmetry about the normal implies that part of the parallel momentum of the incident reagent atom is retained by the product. Such momentum retention is inconsistent with accommodation of the reagent prior to reaction. The dependence of the mean final energy on E_i similarly implies momentum retention. The high translational, vibrational, and rotational energies of the product are also evidence for an ER mechanism, particularly since these high energies are observed at low T_s . The fact that reaction occurs at all at low T_s implies a small activation barrier, again consistent with an ER process.

In order to understand the dynamics of the ER process, we need details of the potential energy surface (PES) for the system. The basic energetics are reasonably well understood. The H–Cl bond energy is about 4.4 eV. The adsorption energy of a Cl atom on Au(111) is about 2.1 eV,²² and the adsorption energy of an H atom on the Cl-covered surface is likely to have a similar value.²⁸ The dissociative chemisorp-

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FIG. 20. Schematic one-dimensional potential energy diagram for the H+CVAu(111) system.

tion of HCl on Au(111) is then expected to be approximately thermoneutral. Figure 20 shows a schematic one-dimensional potential energy diagram for the system. In the case of an ER mechanism, the starting point of the reaction is the H(g)+Cl(a) state, which is about 2.3 eV above the HCl(g) state. The reaction to form gas-phase HCl is therefore exothermic by this amount. In principle, this full energy could end up in the molecular product. The actually energy disposal dynamics will depend on many parameters of the PES, however. One of the most important is the charge state of the adsorbed Cl. Does the adsorbed atom look like -Cl or $-Cl^{-}$? In the latter case, the initial interaction with the H atom will be weak, like that between H and Ar. In the former, the interaction may be much stronger, like that between H and Cl-Cl, say. These two possibilities are indicated by paths A and B on the diagram. For the H–Cl⁻/Au(111) case (path A) very little energy will be released in the entrance channel. For the H-Cl/Au(111) case (path B) the H atom will be accelerated to high kinetic energy prior to colliding with the surface. Between these two extremes, we can imagine intermediate cases, in which the Cl takes a fractional charge, giving a PES in which energy is released in both the entrance channel and as repulsion between the HCl product and the surface.

One might reasonably expect the Cl to be negatively charged, since the Cl atom has one of the highest electron affinities known (3.6 eV). Taking the gold work function as 5.3 eV gives an energy deficit of only 1.7 eV for charge transfer from the metal to the Cl atom. To a first approximation, this energy will be overcome by the charge/imagecharge stabilization energy for Cl atoms closer than about $e^2/(4 \times 1.7) \approx 2$ Å. At high coverages, charge repulsion will favor a low degree of charge transfer, however. In fact, Kastanas and Koel²² have argued that the effective radius of the adsorbed Cl (<1.24 Å) is too small to correspond to Cl⁻. Path B therefore seems more likely.

In discussions of analogous gas-phase reactions, potential energy hypersurfaces of the general form of path *B* are usually referred to as *attractive* surfaces.²⁹ As was first recognized by Evans and Polanyi³⁰ more than 55 years ago, such potentials generally lead to a high degree of vibrational energy in the nascent product. It is easy to see why this form of energy release might apply to the H+Cl/Au(111) system. For an attractive PES, we expect the H atom to have up to 2 eV of translational energy when it strikes the surface. Relatively little translational energy should be transferred to the much heavier Cl atom on the initial collision. The bond extension of the nascent molecule should be quite large, leading to a high degree of vibrational excitation. The initial acceleration of the H atom may also be expected to lead to small H-Cl impact parameters, and thus to low rotational excitation.

For Cl atoms with appreciable negative charge, the dynamics would be rather different. In this case we should expect the H atom to undergo relatively little acceleration prior to collision with the Cl (path A). Having formed a bond, the product would be high on the repulsive wall of the HCl/Au(111) system, and would therefore be accelerated away from the surface. For A + BC reactions, such a potential is referred to as repulsive.²⁹ In general, a repulsive PES will lead to less vibrational excitation than an attractive one. For the case of a light incident atom, even less vibrational excitation is expected because of the so-called "light-atom anomaly," which was first recognized by Kuntz et al.³¹ A light incident atom can get close to its future partner atom before that atom is appreciably accelerated by the repulsive forces. These forces then serve to accelerate the whole new molecule, leading to translational energy rather than vibrational energy. So-called "mixed energy release"²⁹ in which B-C repulsion also couples to A-B vibration, is minimized when atom A is light compared to B and C. In the case of path A, the absence of steering forces in the entrance channel makes large impact parameters possible, but since the relative velocity at impact is low, the initial orbital angular momentum will also be low. For a repulsive PES with a light incident atom, the repulsive energy release is not expected to generate large torques on the departing molecule, even for nonlinear geometries. Let us consider the various measurements in light of these qualitative arguments.

2. Velocity distributions

I have shown that the velocity distributions of the ER TOF distributions can be accounted for by assuming that they are composed of two components. The relative amounts of these components varies with θ_f , as does the overall mean energy (Fig. 8, Table I). Considerable insight into the reaction dynamics can be obtained by converting the velocity distributions of these two components into energy distributions. Figure 21 shows translational energy distributions corresponding to the velocity distributions fitted to components a and b in the region of the peak in the angular distribution. The velocity distributions were assumed to be of the form of Eq. (1b) with $u_0(x) = 2000$ m/s and $\alpha(x) = 500$ m/s, and $u_0(y) = 1100$ m/s and $\alpha(y) = 600$ m/s. These values are typical of the results listed in Table I. We see that the distribution for component x extends to about 2 eV, the full exothermicity of the reaction. We also see that the energy distributions for the two components are displaced by about 0.5 eV. Component a peaks at a little over 0.8 eV, while component y peaks at a little over 0.3 eV. Likewise, component a extends to about 2 eV, component y to 1.5 eV. This difference is close to the vibrational spacing of the HCl molecule, which is just



FIG. 21. Translational energy distributions of the HCl product of the reaction of H atoms with Cl/Au(111) for the Eley-Rideal mechanism. These distributions correspond to velocity distributions of the form of Eq. (1b) with $u_0(x) = 2000$ m/s and $\alpha(x) = 500$ m/s, and $u_0(y) = 1100$ m/s and $\alpha(y) = 600$ m/s, for components x and y, respectively.

under 0.4 eV, as indicated on Fig. 18. I therefore speculate that component x is associated with molecules produced in the ground vibrational state, and component y is associated predominantly with molecules produced in the first vibrationally excited state. The fact that the two components are separated by 0.5 eV rather than the 0.37 eV energy difference between HCl v = 0 and v = 1 suggests that v = 2 product may also contribute to component b. Such a contribution is in fact expected, since we know from the internal-state distribution measurements that HCl(v=2) is produced by the reaction. This interpretation of the TOF distributions is supported by recent calculations of Kratzer for the H+D/Cu(111) system.¹² Kratzer showed that the observed TOF distributions for that system are most likely composed of several separate components corresponding to HD molecules in different vibrational states.

3. Angular distributions

The angular distributions of the ER TOF component (Fig. 4) were found to peak at about 4° from the normal for $E_i = 0.07$ eV and $T_s = 100$ K. Increasing E_i to 0.3 eV increases this offset to about 6° (Fig. 4). The mean energy of about 0.6 eV (Fig. 8) corresponds to an rms velocity of about 1800 m/s for the HCl, compared to about 3700 and 7600 m/s for the incident H atoms at $E_i = 0.07$ and 0.3 eV, respectively. The total momentum of these beams is thus about 20 and 10 times lower than that of the HCl product. Parallel momentum conservation might be expected to deflect the product by about 3° for $E_i = 0.07$ eV, rising to 6° for $E_i = 0.3$ eV, in good agreement with the observations. The asymmetry of the angular distributions is thus consistent with conservation of parallel momentum. Given the widths of the angular distributions and of the velocity distributions of the incident atom and HCl product, this analysis is clearly over simplified, but it does offer a useful qualitative explanation for the deflections.

The angular distributions were found to have a width (FWHM) of about 40° for $E_i = 0.07$ eV and $T_s = 100$ K. Increasing E_i to 0.3 eV causes a slight narrowing, while heating the surface to 300 K causes a slight broadening (Fig. 5). The narrow widths suggest that the surface/molecule repulsion acts primarily along the surface normal. Molecules directed far from the surface normal might not escape the surface, however, owing to collisions with other Cl atoms. I am not able to distinguish between these effects at this time. Careful inspection of the results shown in Fig. 4 reveals that increasing E_i from 0.07 to 0.3 eV results in a narrower angular distribution primarily because intensity in the "backscattered" direction is reduced in the latter case. Comparing the TOF distributions for $\pm 15^{\circ}$ (Fig. 7) we see that the fraction of component y is smaller for the backscattered case. This behavior is reasonable, since one would expect the parallel momentum of the incident atom to deflect slow product molecules more than fast ones. So the narrowing is associated in large part with an increased depletion of slow species in the backscattered direction with increasing E_i . But why should this effect result in a narrowing in the angular distribution? One possibility is that there is a geometric constraint on the maximum exit angle for direct reactions. Then the shape of the angular distribution at large angles would be independent of E_i (consistent with observations) but the backscattered distribution would be shifted towards the specular at higher E_i , leading to a narrowing in the range of final angles.

The broadening with increasing T_s may reflect thermal motion of the Cl atom prior to reaction. At 300 K, the Cl atoms would have a parallel momentum spread of the order 20% of that of the product HCl. This momentum spread translates into an angular spread of about 13°, which is roughly consistent with the observed increase in angular width of ~6°.

4. Rotational distributions

We have seen that the rotational distribution of the HCl product is approximately independent of v (at least for low J's where the distributions for different v can be compared) and roughly consistent with a Boltzmann distribution at 1400 K (Figs. 12 and 15). Although $T_r \gg T_s$, the total energy released into rotation is small. The mean rotational energy of the ER component is ~ 0.11 eV, or about 5% of the available energy. We also noted that the rotational distribution of J=0to 8 in v = 1 is found to be approximately independent of E_i . The energy release into rotation is similar to that observed for the gas-phase reaction $H+Cl_2 \rightarrow HCl(v,J)+Cl^{32}$ In fact, the reported rotational distributions for this reaction are quite similar to those found for the present system. Anlauf et al.³² estimate a mean fraction of energy in HCl rotation for $H+Cl_2$ of 7%. They also find similar distributions for each v state, tailing to zero population above J=15.

The observed rotational distributions are consistent with both paths A and B described earlier in the context of Fig. 20. Small initial angular momentum is expected in both cases. As was mentioned earlier, for repulsive energy release (path A) we expect little acceleration but a wide range of impact parameters. For attractive energy release (path B), we expect high acceleration but small impact parameters (because of focusing effects). In both cases, the product of the impact parameter and the initial relative velocity is relatively small, leading to low initial orbital angular momentum about the impact point. For repulsive energy release, the torque on the departing HCl molecule will also be small, even for nonlinear geometries.

It is instructive to estimate the absolute rotational excitations expected for different models. Considering a simple impulsive collision limit, $E_i = 0.07$ eV at an impact parameter of 1 Å, gives J=4. Averaging over impact parameters and over the velocity distribution of the beam, one obtains a rotational distribution that is approximately Boltzmann, with $T_r \sim 300$ K.³³ To access J = 15 requires an additional acceleration of the H atom up to a total translational energy of about 0.4 eV, if we hold the impact parameter at 1 Å. If focusing effects reduced the impact parameter to 0.5 Å, the total energy would have to be about 1.6 eV, however. Further experiments in which rotational distributions are measured as a function of E_i may help to clarify these dynamics.³³ Now consider repulsive energy release. Imagine that the Cl atom is accelerated by repulsive energy release to 2 eV for an impact parameter of 1 Å. A Cl atom with this energy would have the same velocity that an H atom would have at a translational energy of 0.06 eV, giving $J \sim 4$. In conclusion, the relatively low fraction of energy released into rotation is an inevitable consequence of the kinematics of this system.

5. Vibrational distributions

The vibrational state distribution was found to peak in v=1, with appreciable population of both v=0 and v=2states. Although such vibrational state population inversions have been seen for many highly exothermic gas-phase reactions,^{29,34} I am only aware of one previous report of such an inversion for a gas-surface reaction. Kori and Halpern³⁵ showed that the oxidation of CO adsorbed on oxidized polycrystalline Pt sample leads to a CO₂ with a vibrational state distribution for the asymmetric stretch mode that is peaked close to the (009) level. In contrast, the vibrational state distribution for H₂ issuing from a metal box flooded with H atoms showed no indication of such a population inversion.³ Although the production of HCl v=1 and v=2 indicates significant energy release into vibration, similar gas-phase reactions exhibit a far higher degree of vibrational excitation. The vibrational state distribution of the HCl product of the reaction of H atoms with Cl₂, for example, peaks in $v = 3.^{32}$ I conclude that the PES for H+Cl/Au(111) is qualitatively different from that for H+Cl₂. One possibility is that part of the exothermicity is lost by the incident atom prior to reaction, which could occur if the incident atom undergoes multiple "bounces" prior to reaction. Another possibility is that the nascent HCl product molecule loses vibrational energy as it departs from the surface, by coupling to the adlayer. Both of these explanations seem unlikely, however, given the fact that the angular distributions are quite narrow and peaked at an angle consistent with parallel momentum conservation. A more likely explanation is that the PES is in fact more repulsive than for $H+Cl_2$. In the limit of pure repulsive energy release, almost all product molecules would be confined to

the ground vibrational state. The energy release in this system may be somewhere between paths A and B, then, with a large fraction of the energy being released after the HCl bond has formed.

6. Dependence on T_s

We have seen that the HCl ER product increases dramatically with increasing T_s . These findings are in good agreement with earlier measurements of Lykke and Kay,⁵ whose observations on the HCl(v=1) signal are very similar to ours. Why should the ER reaction probability increase so rapidly with increasing T_s ? It could be that the nature of the surface Cl species changes dramatically with increasing T_s . For example, the degree of charge transfer could change, or the preferred binding site. A structural study of the temperature dependence of the Cl/Au(111) system would be most useful in this regard. Jackson, Persson, and Kay³⁶ have suggested an alternative dynamical explanation for the T_s dependence of the ER probability. They suggest that this probability increases with increasing Cl-surface separation. They speculate that the increase in vibrational excitation of the Cl-surface oscillator with increasing T_s leads to an increase the ER probability. Further calculations are needed to test this model.

7. Overall energetics

The mean translational, vibrational, and rotational energies are respectively 0.61, 0.32, and 0.11 eV. Taking the exothemicity as 2.3 eV, we obtained 0.27, 0.14, and 0.05 respectively, for the fraction of energy released into these modes. Adding up the energies in these degrees of freedom, we see that, on average, the HCl ER product carries away only about 1 eV, or less than half of the available energy. Where does the remaining energy go? There are several possibilities. The H atom could bounce one or more times before reacting, losing energy on each collision. For this to happen, the atom must first be accelerated to an energy equal to a large fraction of the exothermicity prior to collision, requiring an attractive potential (path B of Fig. 20). But even in the Baule limit, an H atom will only transfer about 10% of its translational energy to a Cl atom in a single collision, requiring many collisions to dissipate half of the available energy. If an H atom were to lose up to 1 eV in this manner, it would also very likely lose its parallel momentum. Yet I have shown that almost all of the parallel momentum of the incident atom is required to account for the displacement of the angular distributions in the direction of the normal. So this mechanism for energy transfer to the surface seems unlikely. Another possibility is that the HCl molecule transfers energy to the metal as it is repelled away from the surface. The mass difference again acts against this mechanism. The translational energy transferred to a single Au atom will be less than 20% of that of the HCl, and even less energy will be transferred if the molecule interacts with several Au atoms. In fact Lykke and Kay³⁷ have shown that HCl losses <20% of its kinetic energy in collisions with Au(111). It is difficult to think of any purely mechanical energy transfer mode that can account for half of the available energy without accommodating the parallel momentum. Rather, some form of coupling to electron hole pairs seems more likely. Detailed calculations are needed to resolve this issue.

Another possibility is that the bond energies used to arrive at an exothermicity of 2.3 eV are in error. This value is obtained by subtracting the Cl–Au bond energy from the Cl–H bond energy. Since the latter is known very accurately, any error would have to be with the Cl–Au determination. The Cl–Au bond energy was obtained²⁴ by using the desorption temperature of 793 K, assuming a pre-exponential of 10^{13} . An error of a factor of 100 in this estimation of the preexponential factor would result in a difference of only about 0.3 eV in the Cl–Au energy. A large error in this energy is unlikely then.

B. Langmuir–Hinshelwood dynamics

We have seen that a component of the TOF distributions behaves quite differently from that of the ER component. The dynamical properties of the slow component of the TOF distributions (Figs. 1 and 2) display none of the attributes of an ER process. There is no evidence for retention of parallel momentum, for example. I therefore attribute this component to an LH reaction mechanism. The angular distribution of the associated HCl product is symmetric about the normal and is close to a cosine distribution (Fig. 9). The respective TOF distributions are found to be approximately consistent with a Maxwell–Boltzmann velocity distribution close to T_s (Figs. 2 and 10). Moreover the rotational distributions are also found to be close to Boltzmann at T_s (Fig. 13).

These results indicate that the HCl product is accommodated to the surface prior to desorption. This behavior is not an essential aspect of an LH mechanism. For example, the reaction of D atoms on Cu(111) to form a gas-phase D_2 product occurs via an LH mechanism, but the product leaves the surface at high kinetic energy³⁸ (comparable to that of the ER reaction in this system) with a relatively narrow angular distribution.²¹ The behavior in the D₂/Cu(111) is characteristic of a system in which desorption occurs directly following recombination. The high translational energy and narrow angular distribution indicate that the D₂ product is accelerated by a potential barrier that would serve to inhibit adsorption.³⁸ In contrast, the HCl product of the present study appears to be fully accommodated prior to desorption. In order to understand better the implications of this behavior, we need to consider the range of potential reactions associated with the H+Cl/Au(111) system. Possible reaction mechanisms include:

$$\begin{array}{ccc} H(g) + Cl(a) & \rightarrow HCl(g) & (I a), \\ & \rightarrow HCl(a) & (I b), \end{array}$$

$$H(g) \longrightarrow H(a^*)$$
 (II),

$$\begin{array}{ccc} H(a^*) + Cl(a) & \rightarrow HCl(g) & (III a), \\ & \rightarrow HCl(a) & (III b) \\ H(g) & \rightarrow H(a') & (IV), \\ H(a') + Cl(a) & \rightarrow HCl(g) & (V a), \\ & \rightarrow HCl(a) & (V b), \end{array}$$

$$H(g) \longrightarrow H(a)$$
 (VI),

$$H(a)+Cl(a) \rightarrow HCl(g)$$
 (VII a)

$$\rightarrow$$
HCl(a) (VII b),

$$HCl(a) \rightarrow HCl(g)$$
 (VIII).

Here (g) and (a) refer to gas-phase and adsorbed species, respectively. Reaction I a is the classical ER reaction mechanism, and III is the so-called "hot-precursor" mechanism,² in which the incident atom may lose substantial energy prior to reaction. Reaction VII is the classical LH mechanisms, in which both reagents are fully accommodated. This process is the reverse of dissociative chemisorption. Reaction VII a, leading to HCl(g) product, is the reverse of direct dissociative chemisorption. Reaction VII b, leading to HCl(a) product, together with reaction VIII, is the reverse of precursormediated dissociative chemisorption. In reaction IV, the incident atom becomes fully accommodated to a high-energy site (e.g., on top of a Cl⁻ layer) where part of the atomic adsorption energy is retained. It is seen that at least four different processes can lead to an accommodated HCl. Even for reaction I, a fraction of the product may not desorb directly. Process I b then has both ER and LH character. Reaction occurs directly as the incident atom strikes the surface, but the product is trapped and desorbs only after full accommodation.

The accommodated HCl observed in the present study could thus originate from any one (or more) of several dynamically distinct processes. Measurements of the dynamical properties of the accommodated product can reveal little about the detailed motions leading to its production. We can, however, gain insight into the origin of the slow component of the TOF's from kinetic measurements. It was noted earlier that HCl signals gradually fall with increasing exposure to the H-atom beam, due to removal of Cl. At $T_s = 100$ K, exposing the Cl/Au(111) surface to the H beam until the (ER) signal falls to about 25% of the initial, then flashing the surface to 300 K, causes the signal at $T_s = 100$ K to drop to essentially zero. If we assume that the probability of H atoms reacting with adsorbed HCl molecules is much smaller than for reacting with adsorbed Cl, this observation indicates that H atoms present on the surface at 100 K react and remove Cl as the surface is warmed. This result is consistent with both reactions V and VII. The fact that the HCl product is so well thermalized suggest that the "b" versions apply, followed by desorption (reaction VIII). Direct recombinative desorption would most likely yield a nonthermalized product. No matter whether desorption is direct or not, applying the principle of detailed balance leads to the conclusion that the dissociation of HCl on the Cl/Au(111) surface can occur without an appreciable activation barrier. Since the adsorption probability of HCl on the surface is found to be small, I am led to consider alternative explanations. One possibility is that detailed balance cannot be applied to this system. Indeed, detailed balance should not be applied to reaction V because the reagent H(a') is a metastable species. This reagent would not be present at equilibrium since it has excess energy left over from the partial accommodation of the incident H atom. While detailed balance should not be applied to

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reaction V, it should apply to the desorption step, reaction VIII, suggesting that HCl can adsorb molecularly on the Cl/Au(111) surface without a barrier.

V. SUMMARY AND CONCLUSIONS

The reaction of H atoms with a Cl/Au(111) surface is found to proceed by way of both Eley-Rideal and Langmuir-Hinshelwood mechanisms. The following points have been established.

(i) The ER reaction yields an HCl product with a narrow angular distribution that is asymmetric about the surface normal in a manner that is roughly consistent with parallel momentum conservation. Increasing E_i moves the peak of this distribution further from the normal.

(ii) The mean translational energy of the ER product molecules is about 0.61 eV, or 26% of the available, increasing slightly with increasing E_i .

(iii) The velocity distributions for the ER reaction are composed of at least two components, attributed to molecules in v=0 and v=1 (possibly with some contribution from v=2).

(iv) The vibrational state distribution peaks in v=1. The form varies slightly with T_s , with about 30% in v=0 and 15% in v=2 states for $T_s=600$ K. The mean vibrational energy is about 0.32 eV, or 14% of the available energy.

(v) This vibrational distribution is inconsistent with a simple attractive PES, which would lead to higher vibrational excitation. Either a large fraction of the energy is released as repulsion between the HCl and the surface, or vibrational energy is quenched, possibly by coupling between the departing molecule and the surface.

(vi) The HCl product has a high mean rotational energy, but this energy represents only about 5% of that available. This result is expected because of the low H-atom mass.

(vii) The mean total energy carried away in the HCl product is only about half of that theoretically available. Some kind of coupling to the surface seems likely, possibly to electron-hole pairs.

(viii) The total yield of the ER reaction increases rapidly with T_s , reaching a cross section of about 2×10^{-16} cm² per Cl atom at $T_s = 600$ K.

(ix) The LH mechanism leads to HCl that is fully accommodated to T_s with respect to its rotational and translational energies.

(x) The HCL product of the LH mechanism at 300 K leaves the surface with an angular distribution that follows a cosine function raised to the power of 1.4.

(xi) The LH reaction does not contribute for $T_s < 140$ K, as its rate becomes vanishingly small.

Figure 22 displays an approximate summary of the energy disposal in this reaction. This is the first time that such detailed information has been obtained for an ER reaction. It is hoped that this and future similar studies will ultimately provide insight into the dynamics of ER reactions in general, and that this knowledge will be of value to those persuing the synthetic applications of hot-atom chemistry,^{39,40} many questions remain, however. The biggest weakness of the present study is the absence of detailed structural information on the



FIG. 22. Summary of the energy disposal in the reaction of H atoms with Cl/Au(111) for the Eley-Rideal mechanism. The curve corresponds to the translational energy distribution of the form of Eq. (1b) with $u_0=860$ m/s and $\alpha=900$ m/s, giving a mean translational energy of about 0.6 eV. The squares indicate the populations of the v=0, 1, and 2 levels, plotted against their energies. The triangles give the rotational state distribution.

Cl/Au(111) adlayer, including any temperature dependence. An STM study, for example, could be most informative in this regard. For the ER reaction, we need to understand better how the missing reaction energy is disposed. Is energy being lost to the surface? Or is the thermochemistry badly in error? We would also like to understand the dependence of the cross section on T_s . A dynamical explanation for the variation of the mean translation energy with final angle would also be good. For the LH mechanism, we need to understand exactly which of the processes I–VIII are relevant and to study the kinetics and dynamics of individual steps.

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