I. INTRODUCTION

The reaction of Cl$_2$ with Al(111) involves vertically nonadiabatic charge exchange, remote dissociation, and high velocity neutral atom ejection via direct and precursor-mediated abstractive chemisorption. Kasemo and co-workers' first explored photon and electron emission from halogen/sodium systems. The theoretical groundwork for understanding the mechanism of nonadiabatic charge transfer in similar systems involving electron abstractive chemisorption has been used to demonstrate that the reaction of Cl$_2$ on the low work function Al(111) surface proceeds via a prompt vertical electron harpooning process. Sticking measurements were performed showing that Cl$_2$ adsorbs via a direct chemisorption process at either high incident translation energy or high surface temperature. However, at glancing incident angles and low surface temperatures (100 K), a precursor-mediated channel predominates. REMPI studies show that fast abstracted Cl was produced via both channels: direct, remotely-dissociated incident Cl$_2$, and indirect, precursor-mediated Cl$_2$. For incident Cl$_2$ of 0.11 and 0.27 eV at 40° incident angle and 100 K surface temperature, only the precursor-mediated channel was observed with atomic Cl abstracted product energies of 0.09–0.14 eV. At high surface temperature, 500 K, all incident translational energies and angles yield only the direct channel, with abstracted product energies of 0.19–0.26 eV.

Resonantly enhanced multiphoton ionization (REMPI) and time-of-flight mass spectroscopy have been used to demonstrate that the reaction of Cl$_2$ on the low work function Al(111) surface proceeds via a prompt vertical electron harpooning process. Sticking measurements were performed showing that Cl$_2$ adsorbs via a direct chemisorption process at either high incident translation energy or high surface temperature. However, at glancing incident angles and low surface temperatures (100 K), a precursor-mediated channel predominates. REMPI studies show that fast abstracted Cl was produced via both channels: direct, remotely-dissociated incident Cl$_2$, and indirect, precursor-mediated Cl$_2$. For incident Cl$_2$ of 0.11 and 0.27 eV at 40° incident angle and 100 K surface temperature, only the precursor-mediated channel was observed with atomic Cl abstracted product energies of 0.09–0.14 eV. At high surface temperature, 500 K, all incident translational energies and angles yield only the direct channel, with abstracted product energies of 0.19–0.26 eV.
Using a simple jellium model, it has been shown that the image charge increases the adiabatic electron affinity by $-3.6 \text{ eV}/z (\text{Å})$, where $z$ is the distance between the molecule and the surface in angstroms.\(^{17}\) This image charge shifted adiabatic electron affinity is termed the effective adiabatic electron affinity ($E_{\text{eff}}^\lambda$). Horizontally adiabatic charge transfer from the Cl$_2$ potential minimum to the Cl$_2^-$ potential minimum is shown in Fig. 1(b). This process would require the Cl–Cl bond to stretch on a time scale on the order of the electronic transition. This assumption is not valid: an electronic transition would be much faster than the bond length relaxation. In this case, the Franck–Condon overlap of the Cl$_2$ and Cl$_2^-$ wave functions predicts only a small probability for adiabatic charge transfer.

The high incident velocity allows the Cl$_2$ to move closer to the surface shifting the Cl$_2^-$ curve to even lower energies, again due to image charge stabilization of Cl$_2^-$. As shown in Figs. 1(c) and 1(d), in Fig. 1(c), the Cl$_2$ is sufficiently close to the surface that the Cl$_2$ potential crosses the Cl$_2^-$ potential at the Cl$_2$ potential minimum. The vertical electron affinity is the energy difference between the Cl$_2$ potential minimum and the Cl$_2^-$ potential at constant internuclear separation ($\Delta r=0$). The vertical electron affinity is shifted by $-3.6 \text{ eV}/z (\text{Å})$ near the surface due to Cl$_2^-$ image charge stabilization. This shifted vertical electron affinity is termed the effective vertical electron affinity of the Cl$_2$ ($E_{\text{eff}}^\lambda$). When the molecule is sufficiently close to the surface that the effective vertical electron affinity is equal to the work function of the metal ($E_{\text{eff}}^\lambda = \Phi_A$), a Franck–Condon allowed harpooning event can occur. The distance at which the electron harpoons from the surface to the Cl$_2$ can be calculated using Eq. (2),\(^{17}\)

$$z_{\text{harpooning}} = \frac{3.6 \text{ Å}}{\Phi_A (\text{eV}) + E_{\text{gas}}^\lambda (\text{eV})}.$$  

Using this equation, a vertically resonant harpooning distance between the assumed jellium sea and the assumed hole of 1.1 Å is calculated.

After the charge transfer, the Cl$_2^-$ is formed high on the repulsive portion of its potential. The Cl–Cl bond immediately begins to extend from 1.99 Å (Cl$_2$) to 2.47 Å (Cl$_2^-$). The total energy of the Cl$_2^-$ system resides above the dissociation limit of Cl$_2$. A portion of the excess energy, $E_{\text{excess}}(\text{Cl}_2^-) = E_{\text{after harpooning}}(\text{Cl}_2^-) - E_{\text{accum}}(\text{Cl}_2^-)$, can be channeled into the translational energy of a departing Cl atom.

The most likely scenario leading to hyperthermal Cl atom ejection is a vertically nonadiabatic [Fig. 1(d)] charge transfer. The Cl$_2$–surface distance at which vertically resonant charge transfer occurs can be seen as the threshold for a vertical charge transfer ($E_{\text{eff}}^\lambda (\text{Cl}_2^-) = \Phi_A$): it is the furthest distance at which an electron can harpoon. The high velocity of the incident Cl$_2$ may allow it to approach passed this threshold, creating a highly excited hole at the surface. In the vertically nonadiabatic charge transfer, the effective vertical electron affinity of the Cl$_2$ exceeds the work function of the Al(111) surface ($|E_{\text{eff}}^\lambda| > \Phi_A$). Similar to the case of vertically resonant charge transfer, excess energy can be channeled into the translational energy of a departing Cl atom. Using simple gas phase potentials of Cl$_2$ and Cl$_2^-$,\(^{17}\) we estimate a total excess energy of 0.4 eV for either vertically resonant or vertically nonadiabatic charge transfer [Fig. 1(c) or 1(d)]. Assuming equal partitioning of this energy into each Cl atom, the velocity of the ejected Cl atom is estimated to be 1050 m/s. This simple calculation does not take into regard factors such as incident translational energy, molecular orientation of the impinging Cl$_2$, acceleration of the anion upon harpooning, etc.

The differentiation between vertically resonant and vertically nonadiabatic charge transfer is indeed difficult. The vertical transition from the Cl$_2$ potential to the Cl$_2^-$ potential places the molecule at the same position high on the repulsive portion of the anion potential for both processes, resulting in the same predicted exit translational energy of the ejected Cl atom. The observation of hyperthermal Cl ejection from the surface would indicate that electron harpooning occurs at low coverage; the distinction between vertically reso-

**FIG. 1.** Evolution of Cl$_2$ and Cl$_2^-$ potential energy curves as a function of the Cl$_2$/Al(111) reaction coordinate ($z$). The separation between the Cl$_2$ and the surface ($z$) decreases from the left frame (a) to the right frame (d). (a) Adiabatic charge transfer is endothermic by 1.25 eV at infinite separation. (b) At $z = 2.9$ Å, the wave function overlap predicts small resonant adiabatic charge transfer probability. (c) At $z = 1.1$ Å, vertically resonant charge transfer results in dissociation of Cl$_2^-$ into Cl and Cl$^-$ fragments with the excess translational energy shown between the arrows. (d) At $z < 1.1$ Å, vertically nonadiabatic charge transfer results in the same products and excess energy as the vertically resonant process.
nant and vertically nonadiabatic charge transfer processes is not particularly relevant.

Initial sticking probability on the surface is measured using two different King and Wells-type sticking techniques. Three sets of time-of-flight experiments determine the velocity of ejected Cl atoms from the reaction of Cl$_2$ on the Al(111) surface. Both a direct and a precursor-mediated channel produce hyperthermal product. Using a normal incident Cl$_2$ beam, ejected Cl velocities are measured at three exit angles to show the existence of hyperthermal product ejection. Further experiments performed by varying the incident angle and surface temperature are used to differentiate the direct channel from the precursor-mediated channel.

II. EXPERIMENTAL SET-UP

The reaction dynamics of Cl$_2$ on Al(111) are studied using time-of-flight mass spectroscopy (TOF-MS) with resonantly enhanced multiphoton ionization (REMPI) of scattered atomic chlorine under ultrahigh vacuum (UHV) conditions. The details of the experimental apparatus have been previously published.$^{24-27}$ The set-up for the current experiments includes a tunable light source with a complementary TOF-MS for the detection of ionized incident and scattered product species. The molecular beam source consists of a differentially pumped valve supersonic Cl$_2$ molecular beam directed into the ultrahigh vacuum reaction chamber with a base pressure of $1.8 \times 10^{-10}$ Torr. A standard suite of UHV instruments is also available, including an argon ion sputter gun, a quadrupole mass spectrometer (QMS), an Auger electron spectrometer (AES), and a low-energy electron diffraction instrument (LEED).

REMPI is used to ionize the atomic Cl $3p^2P_{3/2} \rightarrow 4p^52P_{3/2}$ transition at 210.1 nm.$^{28-31}$ The doubled output (532 nm) of a Q-switched Nd:YAG laser (Quantel 581 C-SF) pumps a DCM dye laser (Lambda Physik FL-3002). The 630.3 nm fundamental (Lambda Physik DCM/Fisher Optima methanol) from the dye laser is doubled in KDP-C then tripled in BBO-1, using a pair of Inrad Autotracker III's, to obtain the desired 210.1 nm UV light. The 210.1 nm UV is isolated from the dye fundamental and doubled frequencies using dichroic mirrors and subsequently sent into the reaction chamber. A 370 mJ, 532 nm pulse from the Nd:YAG laser produces 55 mJ of 630.3 nm dye fundamental and 1.5 mJ of 210.1 UV, with pulse widths of <7 ns.

Using a 20 cm focal length lens, the laser is focused into the chamber in an orientation orthogonal to the molecular beam path. The lens is mounted off axis in a rotatable barrel which allows the laser focus to be positioned in the molecular beam path or rotated in an arc around the dose spot on the sample for angular dependent detection of scattered products. The diameter of the arc (1.41 ± 0.03 cm) of the laser focus is controlled by the radial position of the lens from the center axis of the barrel. For experiments reported in this manuscript, the detection laser is rotated from 15° to 35° relative to normal incidence.

The skimmed and chopped (∼15 μs pulse width, 10 Hz) diatomic chlorine molecular beam is created using a pulsed valve (General Valve, model 9-400-900 2 mm orifice) in a triple differentially pumped source chamber and directed at the surface at three incident kinetic energies: pure Cl$_2$ (0.11 ± 0.02 eV), Cl$_2$ seeded in Ne (0.27 ± 0.01 eV), and Cl$_2$ seeded in He (0.65 ± 0.01 eV). Chlorine is purchased pre-mixed with He (Cl$_2$ 5.32%/He balance) and Ne (Cl$_2$ 5%/Ne balance) from Matheson. Pure chlorine is also purchased from Matheson. No contamination by other halogens is detected by QMS.

Standard surface preparation techniques are employed to clean and characterize the Al(111) surface. The surface is prepared by 2 kV Ar$^+$ ion sputtering followed by electron beam annealing at 773 K for 2 min. The surface dosing follows immediately after verification of cleanliness by AES. Surface order is checked by LEED.

The Al(111) crystal is maintained at one of three temperatures by cooling the surface to 100 ± 3 K using liquid nitrogen, cooling to room temperature (300 ± 3 K) using an air line, or heating to 500 ± 5 K using radiative heating. Three surface orientations (0°, 20°, 40°) with respect to the incident beam are used. Varying the surface temperature and orientation allows for differentiation between the direct and precursor-mediated abstractive chemisorption mechanism for Cl$_2$ on Al(111).

A thermionics time-of-flight mass spectrometer is mounted on a rotatable flange. The spectrometer is a standard two grid accelerator, two-pole aspherical lens steered TOF-MS. The length of the flight tube is 10 cm. The TOF-MS is tilted toward the surface (45°) to maximize the signal of the scattered products.

The velocity of the incident beam from the chopper to the surface (v$_{CS}$) is measured using a UTI 100C quadrupole mass spectrometer. The TOF and pulse profile of the incident Cl$_2$ is measured daily using the laser TOF-MS method. These checks are performed to verify that the incident velocity is consistent with the QMS value and to ensure that the arrival time of the incident Cl$_2$ at the surface (t$_{CS}$) is consistent between experiments. For example, the t$_{CS}$ of the incident Cl$_2$/He is 116.7 ± 0.3 μs for 19 random samples, indicating that we have experimental control of the incident beam. This time (t$_{CS}$) is the zero time of the ejected product time-of-flight. The window of ion collection for the determination of product velocities is at most 50 μs from t$_{CS}$. No signal is seen after 6 ms. We are not able to measure long lived precursors since any long-lived desorption states would have negligibly small signals. For example, if the precursor lifetime was 5 ms, the precursor desorption signal would be 100 times smaller than the scattered signal and therefore undetectable.

The initial sticking probability of Cl$_2$ on Al(111) is measured using two King and Wells-type sticking experiments. For both experiments, a movable Pyrex flag is used to block the molecular beam both prior to and after surface dosing. A gate valve blocks the molecular beam for background measurements. A standard sticking experiment set-up uses the QMS analog output to a National Instruments LabView Virtual Instrument to monitor the partial pressure of Cl$_2$. A peak-to-peak sticking experiment is performed using a QMS and a Tektronix TDS 3052 oscilloscope.

The velocity of the ejected Cl atoms is determined using the TOF of the neutral reaction products from the surface to
the laser focus. The distance from the surface dose spot to the detection laser is checked weekly.

III. RESULTS

Two different types of time-of-flight spectra characterize the scattered products. First, neutral TOF spectra are recorded by increasing the delay between the chopper trigger and the laser trigger by small increments (typically about 2–3 $\mu$s). These spectra quantify the flight time of the scattered products from the surface to the laser focus. Second, analysis of the ion TOF, defined as the flight time from the laser focus to the TOF-MS electron multiplier, probes the mass of the species present in the scattered signal.

Four distinct species constitute the observed scattered atomic chlorine TOF spectra. The contributions of each of these components to the total scattered Cl atom signal are independently characterized. The components include: Cl from aluminum chloride etch products [Eq. 3(a)], Cl from the photodissociation of inelastically scattered Cl$_2$ [Eq. 3(b)], direct abstracted Cl from remotely dissociated incident Cl$_2$, and indirect abstracted Cl from precursor-mediated chemisorption of Cl$_2$ [Eq. 3(c)]. We justify the proposed bimodal abstraction reaction of Cl$_2$ on Al(111) by confidently accounting for the etch products and inelastically scattered Cl$_2$.

A. Etch

A typical neutral species TOF spectrum which displays normalized ion intensity vs flight time from the surface ($\mu$s) is shown in Fig. 2(a). The total Cl$^+$ signal (C) is predominantly composed of atomic chlorine from the direct harpoon and indirect precursor-mediated harpooning reactions along with photodissociated chlorine from the slower aluminum chloride etch products. The results of numerous research groups show that these etch products are primarily Al$_2$Cl$_6$ (below 450 K) and AlCl$_3$ (500–700 K). 32–37 A complementary Al$^+$ TOF spectrum (C) is recorded for each Cl signal. Because the MPI detection of Al$^+$ is much less efficient than the REMPI detection of Cl$^+$, the Al$^+$ signal is scaled to fit the Cl$^+$ signal at long times. At long times, both the Cl$^+$ and the Al$^+$ signals originate from etch products. Subtraction of the well-separated Al$^+$ etch signal from the total Cl$^+$ signal allows us to obtain the hyperthermal abstracted components of the Cl signal (solid line).

B. Inelastic

Several techniques determine that the source of Cl$^+$ signal originates predominately from atomic Cl, not from molecular Cl$_2$. At early arrival times [Fig. 2(b)], the ratio of atomic chlorine to molecular chlorine (Cl:Cl$_2$) is 310:1. A Cl:Cl$_2$ ratio of 50:1 is measured for molecular chlorine inelastically scattered from an inert aluminum oxide surface. This indicates that even with the most conservative estimates and the assumption that one count of Cl$_2$ signal results in 50 counts of atomic Cl in pure inelastically scattered Cl$_2$, a minimum of 80% of the atomic chlorine signal results solely from abstracted Cl$_2$ product. Further data supports up to 95% hyperthermal Cl at early arrival times.
Upon exposing the surface to Cl$_2$, steady state sticking of atomic Cl signal seen at early times separated in time that it does not add appreciably to the sensitive to Cl$_2$. However, this Cl$_2$ signal is sufficiently well-separated in time that it does not add appreciably to the atomic Cl signal seen at early times (<20 μs).

The incident angle of the molecular beam is also used to separate the inelastically scattered Cl$_2$ from the atomic Cl. At glancing incident angles, the detection of the inelastic collisions of Cl$_2$ on the Al(111) surface can be eliminated since the inelastically scattered products leave the surface at specular angles. The fast ejected Cl product should leave the surface along the surface normal, regardless of incident angle. Upon verification that the Cl velocities are nearly identical at forward and backscattering angles, we assert that the ejected Cl signal primarily arises from ejected Cl atoms and not from the photodissociation of inelastically scattered Cl$_2$.

C. Hyperthermal Cl product

1. Sticking experiment

Standard King and Wells reflection technique sticking experiments$^{38,39}$ using a QMS to monitor the partial pressure of Cl$_2$ exhibits very poor signal to noise because the chamber walls of the large reaction vessel act as efficient Cl$_2$ pumps. Upon exposing the surface to Cl$_2$, steady state sticking of only ~70% is initially seen at low surface temperature ($T_S$ = 100 K) and low incident energy (<0.2 eV) followed by an abrupt transition to saturation of the surface [Fig. 3(a)]. The initial sticking measurements, under other conditions [$E_{\text{inc}}$(Cl$_2$) = 0.11 eV at $T_S$ = 300 K or $E_{\text{inc}}$(Cl$_2$) = 0.27 eV at $T_S$ = 100 K], behave as expected for continuous etching as shown in Fig. 3(b). For $E_{\text{inc}}$(Cl$_2$) < 0.2 eV at $T_S$ = 100 K, we expect saturation starting when the flag is withdrawn [Fig. 3(a)]. Instead, the saturation has a 20 s induction time. Barenbak et al. have observed this previously and ascribe it to desorption of gas from the chamber walls closest to the quartz flag. This indicates that the real sticking at $E_{\text{inc}}$(Cl$_2$) < 0.2 eV at $T_S$ = 100 K is >70%.

A transient peak-to-peak sticking method (Fig. 4) accommodates the fast pumping of Cl$_2$ between molecular beam pulses and accurately measures the sticking probability at low surface temperature and low incident energy. At all other surface temperatures and incident energies, the measured sticking is the same for both techniques providing the validity of the transient peak-to-peak method. The fast oscilloscope records the QMS signal while the molecular beam is run at 2 or 5 Hz to lower the dose rate. Several peaks, taken while the flag blocks the beam path (Fig. 4, 1–6), are averaged to obtain a baseline for each run. Note the immediate decay of each peak, indicative of very fast chamber pump-
ing. The values for initial sticking after the flag is removed (Fig. 4, 7–21) and for background verification after the flag is replaced (Fig. 4, 22–25) are both obtained by a similar peak averaging method. A statistical analysis is made possible by multiple runs taken at each set of conditions.

The initial sticking probability vs surface temperature and incident kinetic energy (Fig. 5) supports the assertion that a precursor state exists at low surface temperature ($T_S = 100$ K) and low incident energy $Cl_2 (<0.2$ eV). The incident kinetic energy of the $Cl_2$ is varied by seed gas and by tilting the surface. For high incident energy $Cl_2 (0.50–0.65$ eV), the sticking probability is independent of surface temperature ($\sim 60\%$). At low incident energies, surface temperature gives rise to a pronounced effect: sticking probabilities between 20%–40% are measured at 300 and 500 K surface temperatures. However, low temperature and low incident kinetic energy conditions enhance the sticking to 80%–100%, indicating a molecular precursor.

2. Exit angle experiment

From the pure hyperthermal abstracted Cl product TOF spectra, velocities are obtained. The most probable arrival time is defined as half of the full width half maximum plus the arrival of the leading edge half maximum. The velocity of the ejected Cl atoms is measured as a function of (1) exit angle, (2) incident angle, and (3) surface temperature.

Our simple model predicts that the direct channel should produce ejected product along the surface normal and the velocity of the ejected Cl from the direct channel should be independent of incident $Cl_2$ kinetic energy. Detection of high velocity Cl along the surface normal is an indication of a vertical electron transfer process. Other factors which may influence the exit angle and energy of the ejected Cl include the orientation of the impinging $Cl_2$ molecule with respect to the surface normal, the acceleration of the $Cl_2$ anion post harpooning, and the partitioning of the $Cl_2$ dissociation energy. These will be discussed further in Sec. IV A.

Figure 6 shows the laser/surface orientations for the exit angle measurements. For these experiments, the high and low incident energy $Cl_2$ are directed along the surface normal and the laser focus lens is rotated to 15°, 22°, and 35° detection angles. Exactly normal detection of scattered product during normal incident dosing is impossible due to the large intensity of the incident beam; therefore, the detection laser is placed just outside of the incident beam (15° with respect to the surface normal).

The energy of abstracted Cl is independent of exit angle (15°–35°) and incident $Cl_2$ energy at 100 K surface temperature (Fig. 7, left axis, solid symbols). Incident $Cl_2$ beams of 0.11 eV ($\unicode{A1}$), 0.27 eV ($\bullet$), and 0.65 eV ($\bigcirc$) all produce ejected Cl of $0.21\pm0.03$ eV. This observed Cl energy is nearly half of the 0.4 eV total excess energy estimated earlier using only simple gas phase potentials. This fortuitous result depends upon highly complex factors. However, the independence of the exit energy on the exit angle at near-normal exit angles is consistent with the simple model of electron harpooning shown in Fig. 1.

A plot of velocity vs exit angle (Fig. 7, right axis, open symbols) demonstrates the hyperthermicity of the ejected Cl. For all $Cl_2$ incident energies and exit angles, a mean velocity of $1045\pm27$ m/s is measured for 100 K Al(111). This mean was calculated using 68 samples and the error bound used is the standard error. The ratio of the mean product velocity vs the full width at half maximum (FWHM) of the TOF is a good metric upon the relative width of the velocity distribution. A thermal flux-weighted Maxwell–Boltzmann distribu-
tion exhibits a 1:1 ratio between the most probable velocity and the FWHM. However, the mean velocity to FWHM of the 0.65 eV normal incident beam from a 500 K surface yielded a ratio of \( \sim 0.84 \), indicating a relatively broad velocity distribution. This ratio will be compared to the ratio found for the precursor channel in Sec. IV B. The mean velocity of Cl product exceeds the incident velocity of Cl\(_2\)/Ne and pure Cl\(_2\) using all exit angles. For example, the velocities of the ejected Cl from incident Cl\(_2\)/Ne (850 m/s) and pure Cl\(_2\) (535 m/s) are accelerated to 1006 and 1164 m/s, respectively. As explained in the Introduction, assuming a simple vertical transition between the gas phase Cl\(_2\) and the work function/image shifted Cl\(_2^+\) potentials with equal partitioning of the excess energy into the two fragments, we estimate a Cl exit velocity of 1050 m/s. The experimental data is consistent with a vertical electron harpooning mechanism.

### 3. Fixed laser experiment

The surface/laser orientation for incident/exit angle and surface temperature experiments is shown in Fig. 8. For these experiments, the laser focus remains at 15° with respect to the incident molecular beam. The purpose of this experiment is to determine the effect of incident angle. As the surface is tilted from normal to 20° to 40°, detection at 15°, 25°, and 25° exit angles is a consequence of fixing the laser focus.

Tilting the surface while holding the laser position fixed results in detection of the product at a backscattered angle, thereby reducing the sensitivity to inelastically scattered Cl\(_2\). At 20° incidence [Fig. 8(b)], the detection angle is \(-5°\), and at 40° incidence [Fig. 8(c)], the detection angle is \(-25°\). The exit angle of hyperthermal products resulting from a nonadiabatic electron harpooning mechanism should not be a function of incident angle and should produce backscattered Cl.

Figure 9 shows the translational energy of the abstracted Cl product, \( E_{\text{trans}}(\text{Cl}) \), vs the translational energy of the incident Cl\(_2\), \( E_{\text{trans}}(\text{inc}) \), at three sets of surface orientations and 100 K surface temperature. At 0°/15°, the exit translational energy \((0.21 \pm 0.01 \text{ eV})\) of the ejected Cl atom is independent of incident kinetic energy (0.11–0.65 eV). At glancing incident angles (20° and 40°), the energy of the ejected Cl is less than for normal incident Cl\(_2\) beams and the exit energy of the Cl is a function of incident energy. At 40° incident angle, 0.65 eV incident Cl\(_2\) resulted in 0.17 \pm 0.01 eV, 0.27 eV incident Cl\(_2\) resulted in 0.14 \pm 0.02 eV, and 0.11 eV incident Cl\(_2\) resulted in 0.09 \pm 0.02 eV. Note that even for...
the lowest exit Cl energy ($E_{\text{inc}} = 0.11 \text{ eV}$, $\Phi_{\text{inc}} = 40^\circ$) the exit Cl is accelerated vs the incident Cl$_2$ from 535 m/s to 690 m/s.

The distinct behavior of the ejected Cl from glancing incident angle Cl$_2$ indicates a separate reaction channel between high and low incident energy Cl$_2$. The energy of the abstracted Cl products is reduced from $\approx 0.21 \text{ eV}$ to $\approx 0.10 \text{ eV}$ when the surface is tilted from normal to 40° incident angle for 0.11 eV Cl$_2$. Trapping in precursor states often scales with the normal component of the incident energy.$^{42}$ Tilting the surface lowers the normal component of the incident energy, thereby increasing the precursor channel at the expense of the direct channel. We propose that one abstraction channel is direct and the second abstraction channel is precursor-mediated.

4. Surface temperature experiment

The surface tilt experiment is repeated at high $T_S$ of 500 K. The same 0.65 eV [Fig. 10(a)], 0.27 eV [Fig. 10(b)], and 0.11 eV [Fig. 10(c)] incident energy Cl$_2$ beams are used. Comparison of the 100 K and 500 K surface tilt data shows clear differences at glancing incident angles. For 0.65 eV incident Cl$_2$ [Fig. 10(a)], the Cl exit energy is nearly independent of both surface temperature and exit angle, which is consistent with a direct chemisorption mechanism. However, for 0.11 eV incident Cl$_2$ [Fig. 10(c)], at glancing incident/exit angles, the Cl exit energy increases by a factor of 2 when increasing the surface temperature from 100 K to 500 K. A similar, though less pronounced, effect is seen for 0.27 eV incident Cl$_2$. This is consistent with the existence of two chemisorption mechanisms for low energy Cl$_2$. Elevated surface temperatures remove the trapping channel for Cl$_2$; therefore, only the direct abstracted product is seen. In the sticking experiment, low surface temperature and low incident energy enhance the sticking of Cl$_2$ on Al(111) consistent with a precursor state. Lower energy ejected Cl from the precursor-mediated channel scales with both surface temperature and normal incident energy.

IV. DISCUSSION

A. Direct abstractive chemisorption

A simple model is proposed for the abstractive chemisorption of Cl$_2$ on Al(111) at low coverage. (1) The hyperthermal velocity of the ejected Cl is indicative of a vertical electron harpooning event. (2) The velocity of the direct channel is independent of incident parameters at most conditions. (3) A precursor-mediated channel is enhanced at low surface temperature and low incident energy.

As the Cl$_2$ approaches the Al(111) surface, the dominant reaction at most experimental conditions is direct, abstractive chemisorption. This mechanism is similar to that proposed by NNL, with the exception that only one electron is transferred, leading to neutral ejection. In Fig. 11(a), an incident Cl$_2$ molecule approaches the surface with varied translational energy. At a distance dependent upon the work function of the Al(111) metal surface and the vertical electron affinity of the Cl$_2$ in the gas phase [Eq. (1)], an electron may tunnel through vacuum to the Cl$_2$. When Cl$_2$ is suddenly converted to the molecular Cl$_2^-$ ion, a positive image charge is created on the surface [Fig. 11(b)].

FIG. 10. Exit Cl translational energy ($E_{\text{exit}}$) as a function of incident Cl$_2$ translational energy ($E_{\text{inc}}$), incident angle ($\Phi_{\text{inc}}$), and surface temperature ($T_S$). $E_{\text{exit}}$ is a weak function of $T_S$ for 0.65 eV $E_{\text{inc}}$ Cl$_2$. For 0.11 eV and 0.27 eV $E_{\text{inc}}$ Cl$_2$ at $\Phi_{\text{inc}} = 20^\circ$ and 40°, increasing $T_S$ from 100 K to 500 K removes the low $E_{\text{exit}}$ precursor channel.

FIG. 11. Schematic diagram of direct, vertical electron transfer. (a) Cl$_2$ impinging on surface. Electron harpoons to proximal Cl. (b) Image stabilization/acceleration. (c) Remote dissociation followed by abstraction of Cl$^-$ and hyperthermal ejection of Cl into the gas phase.
The electrostatic attraction between the anion and the image charge on the surface accelerates the Cl$_2$ toward the surface. Simultaneously, rapid dissociation of the Cl$_2$ anion occurs as it is accelerated toward the surface. The dissociation is driven by the placement of the Cl$_2$ high on the repulsive wall of the Cl$_2$ potential energy curve following the vertical transition from the neutral Cl$_2$ potential energy curve [Fig. 1(d)]. The result is shown in Fig. 11(c). The resulting Cl$^-$ anion from the remote dissociation continues toward the surface and chemisorbs. The neutral fragment Cl atom is ejected from the surface at velocities which can exceed the velocity of the incident Cl$_2$.

This simple model is complicated by the orientation of the impinging Cl$_2$ molecule with respect to the surface normal, the acceleration of the Cl$_2^-$ anion post harpooning, and the partitioning of the Cl$_2$ dissociation energy. The effect of orientation on abstractive chemisorption has been calculated by Binetti et al. for O$_2$/Al(111); similar effects should occur for Cl$_2$/Al(111). For side-on impinging Cl$_2$ being harpooned, the energy released in the dissociation of the Cl and Cl$^-$ is most likely directed parallel to the surface, nearly precluding abstractive chemisorption because escape from the surface of either the Cl or Cl$^-$ cannot proceed without energy directed along the surface normal.

End-on impinging Cl$_2$ is likely to result in hyperthermally ejected Cl and is shown in Fig. 11. In this configuration, as the Cl$_2^-$ breaks apart, it is likely that the charge remains on the halogen atom closest to the surface because it will have the strongest attraction to its image charge. Brandt et al. have experimentally demonstrated that orientation of the N$_2$O with the O-end toward the surface greatly enhances exoelectron emission and N$_2$ scattering in the N$_2$O/Cs$_{12,44,45}$ and N$_2$O/Li$_{12,44,45}$ systems. Harpooning of an electron from the metal surface to the O atom leads to dissociation of the N$_2$O into O$^-$ and N$_2$ fragments. The O$^-$ fragment is accelerated toward the surface by its image charge leading to exoelectron emission. The N$_2$ fragment scatters back into the gas phase. N-end impinging N$_2$O places the O atom sufficiently far from the surface to drastically reduce the harpooning probability. Similarly, it is likely that end-on Cl$_2$ impinging upon the Al(111) surface produces an anionic Cl$^-$ directed at the surface and a neutral Cl directed away from the surface.

For the direct chemisorption channel, the sticking probability is activated. This is quite surprising. Instead, one would expect that when the Cl$_2$ approaches the surface, all of the molecules would undergo harpooning and subsequently either dissociate or abstractively chemisorb. A similar counterintuitive result is observed for the O$_2$ chemisorption on Al(111) via electron harpooning: the chemisorption of O$_2$ is activated and very small (<1%) at low translation energy. For O$_2$, the activated chemisorption cannot be explained with a simple adiabatic model. Instead, Binetti et al. show that the activation barrier is due to the charge transfer being nonadiabatic, very close to the surface, and a strong function of molecular orientation. While an end-on orientation is most favorable for charge transfer, as the incident energy increases, the range of angles increases for charge transfer so the sticking probability increases. Binetti et al. explain that incident translational energy increases charge transfer because as the molecule approaches the surface (a) its bond becomes elongated providing better overlap with the negative molecular ion potential and (b) the neutral can become reoriented during its collision with the surface into a more favorable orientation for charge transfer. Elongation and re-orientation are significant because charge transfer occurs when the O$_2$ is so close to the surface that the gas-surface potential is repulsive.

Compared to O$_2$, charge transfer to Cl$_2$ should occur slightly further from the surface since Cl$_2$ has a larger vertical electron affinity; therefore, one must be cautious in assuming an identical mechanism for Cl$_2$ in the absence of calculations. However, Katz et al. have modeled the charge transfer to I$_2$ during collisions with diamond which should occur further from the surface than charge transfer between Cl$_2$ and Al(111). They observe an exponential increase in charge transfer events with incident translation energy if the charge transfer occurs when the molecule is on the repulsive portion of the gas-surface potential. This strongly suggests that the Cl$_2$ direct sticking probability is activated because charge transfer occurs on the repulsive portion of the gas-surface potential. Our simple jellium model calculations show that resonant vertical charge transfer occurs at only 1.1 Å from the surface so it is not unreasonable that charge transfer occurs on the repulsive portion of the gas-surface potential.

B. Precursor-mediated abstractive chemisorption

At low surface temperature and low Cl$_2$ incident translational energy, a precursor-mediated channel is observed [Fig. 12(a)]. The experimental data that prove the existence of a second abstractive chemisorption channel via a precursor state are: (a) the sticking probability increases with decreasing surface temperature at low incident translation energy and (b) at low surface temperature and low Cl$_2$ incident translation energy, the ejected Cl atoms have a lower kinetic energy than for direct abstractive chemisorption. We propose that the precursor state is trapping into a shallow physisorption well. In contrast to the direct mechanism, where the electron harpoons to the incident Cl$_2$ as it approaches the Al(111) surface, the precursor-mediated charge transfer [Fig. 12(b)] proceeds after adsorption to the surface in a loosely bound physisorption state. Recently, Yourdshahyan et al. have performed DFT calculations which propose a similar precursor-mediated mechanism in the O$_2$/Al(111) system. The distance of van der Waals bonding is equal to or greater than the harpooning distance. Since the van der Waals forces are weak and should not strongly affect the Cl$_2$ potentials, we propose that electron harpooning can proceed after physisorption. Cl$_2$ physisorbed on the surface is expected to reside in a side-on configuration. Cl$_2$ chattering vibrations or other perturbations on the surface could rapidly lead to the preferred end-on configuration for charge transfer. Since the range of orientations for Cl$_2$ undergoing precursor-mediated abstractive chemisorption is very likely to be distinct from Cl$_2$ undergoing direct abstractive chemisorption, it is reasonable that the two channels should have distinct velocity distributions.
The ratio of the mean product velocity to the FWHM of the TOF for both direct and precursor channels also exhibit distinct behavior. The mean velocity to FWHM of the 0.11 eV incident beam at 40° incident angle from a 100 K surface yielded a ratio of ~1.38. This narrow distribution indicates either that a narrow range of orientations produce hyperthermal ejected product or that the electron harpoons onto a shallow portion of the Cl\textsuperscript{2−} potential. In contrast, the ratio of ~0.84 for the direct channel indicates a broad distribution. This difference in mean velocity to FWHM is consistent with the existence of distinct direct and precursor-mediated mechanisms.

The work of several groups suggest that Cl\textsubscript{2} molecular precursors exist on the Al surface. However, since only stable precursors can be experimentally probed, these experiments usually only observe the ionisorption states. Smith\textsuperscript{53} has shown that Cl\textsubscript{2} adsorbs in a molecular precursor state prior to dissociation and subsequent atomic Cl adsorption on vapor deposited Al films. Bermudez and Glass\textsuperscript{54} elaborated on Smith’s work by measuring the work function change of the Al(111) surface vs Cl\textsubscript{2} exposure. They suggested that negative Cl\textsuperscript{−} or Cl\textsubscript{2−} species are formed above the surface. In a similar system, Shi and Jacobi report the existence of O\textsubscript{2−} on the Cs/Ru(0001) surface.\textsuperscript{55}

Precursor-mediated charge transfer has been seen in the O\textsubscript{2} on oxygen precovered, Cs-covered Ru(0001) system at high oxygen coverage by Grobecker and co-workers.\textsuperscript{5,9} We propose that in the Cl\textsubscript{2}/Al(111) system, hyperthermal atom abstraction can proceed via a similar precursor-mediated channel with the caveat that the sticking probability data strongly suggests that the Cl\textsubscript{2}/Al(111) precursor is a physisorption state. No long time Cl atom ejection is seen in contrast to the very long persistence of exoelectron emission in O\textsubscript{2} on oxygen precovered, Cs-covered Ru(0001). This is consistent with our hypothesis that the precursor for abstraction chemisorption of Cl\textsubscript{2}/Al(111) is a metastable physisorption state, not a long-lived ionisorption state.

Although there are no published calculations for Cl\textsubscript{2}/Al(111), Weisse et al.\textsuperscript{56} have calculated a model for O\textsubscript{2}/Al(111) to fit the experimental data of the sticking probability for O\textsubscript{2}/Al(111). Weisse et al. proposed that there is a shallow (0.1 eV) well outside the activation barrier to dissociation which affects the angular dependence of the sticking probability. Because charge transfer probably takes place on the repulsive portion of the O\textsubscript{2}/Al(111) potential, it is reasonable that a physisorption well exists at a greater distance from the surface. For Cl\textsubscript{2}, the charge transfer also probably occurs on the repulsive portion of the potential because the direct sticking probability is activated, therefore it is also reasonable that a physisorption well exists.

Although our data is consistent with a physisorption precursor, the temperature dependence of the sticking probability of Cl\textsubscript{2}/Al(111) at low surface temperature could be due to energy dissipation and stabilization of Cl\textsubscript{2−}. Because Cl\textsubscript{2−} is a stable molecular ion, if the Cl\textsubscript{2} bond were stretched by the interaction with Al(111), it is possible that a vertical electron transfer would occur to a region of the Cl\textsubscript{2} potential below the vacuum level. This could create metastable Cl\textsubscript{2−} on Al(111). In the absence of physisorption, it is difficult to see how raising the surface temperature would decrease sticking and increase inelastic scattering even if metastable Cl\textsubscript{2−} formation occurs. However, the work of Katz et al.\textsuperscript{57} for O\textsubscript{2} on Al, Cs, and Ag shows that the seam crossing between the neutral and ionic potentials are complicated and that re-crossing can occur. Therefore, it is hard to completely eliminate the possibility that our data for Cl\textsubscript{2}/Al(111) sticking is consistent with a Cl\textsubscript{2−} precursor state. However, we feel that it is reasonable to assume that the increase in sticking probability at low-incident energy with decreased surface temperature is most conservatively explained by a Cl\textsubscript{2−} physisorption state, and this is consistent with the most recent calculations and data for O\textsubscript{2}/Al(111).\textsuperscript{56}

C. Comparison to other abstraction studies

In addition to previous work by Kummel and co-workers,\textsuperscript{26,27,58–62} halogen atom abstraction has been seen in the F\textsubscript{2}/Si(100)-(2×1) system by Li et al.\textsuperscript{19} and in the Cl\textsubscript{2}/K system by Strömquist et al.\textsuperscript{20} Notably, Tate et al.\textsuperscript{21,22} have reported that the reaction of F\textsubscript{2} on the Si(100) surface exhibits hyperthermal neutral ejection. F\textsubscript{2} molecules impinging upon the Si surface at 395 m/s produced scattered F atoms with velocities of 1195 m/s. However, the energy for this hyperthermal ejection has been ascribed to the formation of a single Si–F covalent bond and the subsequent repulsion of the second F atom, not harpooning.\textsuperscript{63}
D. Conclusion

The reaction of Cl\textsubscript{2} on the Al(111) surface proceeds via a vertical electron harpooning mechanism. Following the electron transfer, one Cl atom is chemisorbed on the surface while the other Cl is ejected into the gas phase. The measured velocity of this atom far exceeds the velocity of the incident Cl\textsubscript{2}, consistent with a vertical electron-harpooning mechanism. Moreover, two distinct reaction pathways are capable of producing hyperthermal Cl. The direct abstructive chemisorption can result in ejected Cl velocities which are twice that of the incident Cl\textsubscript{2}. A secondary process also results in hyperthermal Cl ejection from a precursor-mediated channel.