I. INTRODUCTION

There has been much interest and activity over the past decade in the interaction of hydrogen atoms and molecules with graphite and other chemically similar forms of carbon (SWNT, graphene, etc.). Much of this interest is stimulated by the possibility of using one or the other forms of C as a hydrogen storage material and for its role in the formation of molecular H2 in the interstellar medium. The latter process is generally believed to occur via recombination of H atoms on dust grains1 that are principally either silicates or graphite-like, e.g., graphite onionlike particles or polycyclic aromatic hydrocarbons.2

It was originally suggested in electronic structure calculations,3,4 and subsequently confirmed experimentally,5 that H atoms incident from the gas phase can weakly chemisorb over an atop site on the C(0001) terrace by breaking some of the π bonding and puckering the atop C out of the plane. From density functional theory (DFT) calculations, the binding energy of a single H atom to the basal plane of C(0001) is ~0.7 eV, with a C atom puckering of ~0.4 Å and with a barrier to entrance into the chemisorption well of ~0.2 eV from gas phase H+C(0001).4 Scanning tunneling microscopy (STM) experiments6,7 and DFT calculations8 demonstrate that barriers to H adsorption are small or negligible for some configurations of the larger clusters, as well as for formation of the dimer, and therefore larger clusters are readily produced via increased H exposure. The calculations9 show that the average H binding energy increases with cluster size and this provides a thermodynamic driving force for the formation of large clusters at higher \( \Theta_H \).

At higher \( \Theta_H \), STM experiments see larger and more complex clusters as well as dimers.8,7 In the limit of saturation coverage, \( \Theta_H \sim 0.4 \),9 atomic resolution is entirely lost so that the underlying C lattice is not even visible.8,7 DFT calculations8,10 demonstrate that barriers to H adsorption are moderate large (>1 eV), but that the barrier to H adsorption into the dimer configurations relative to the monomer adsorption is <0.2 eV or even nonexistent.8 Thus, the latter is the predominate reason for formation of dimers at low \( \Theta_H \).

We previously measured the internal state averaged translational energy distribution of H2 (D2) associatively desorbing from a H(D) saturated C(0001) surface.11 These experiments measured the time of flight (TOF) for the associ-
tively desorbed H\(_2\) (D\(_2\)) induced by a pulsed IR laser T-jump of the surface. Broad translational energy distributions normal to the surface were observed, peaking at \(\sim 1.3\) eV and extending to \(\sim 3.4\) eV, the energetic limit calculated via DFT for associative desorption from the para dimer configuration. It was not, however, possible to determine whether the modest average translational energy observed (relative to that available) and the large breadth of the distribution were caused by populating many internal states in the associative desorption, a broad lower distribution in available desorption energies due to variations in barriers to associative desorption (relative to the dimer), or a large and broad distribution in energy loss to the surface in the desorption process. The angular distribution for the associative desorption was highly peaked normal to the surface and no isotope effect was observed.

To date, no atomic H or D desorption from C(0001) has been directly observed. Only associative H\(_2\) (D\(_2\)) desorption is observed in TPD experiments at all \(\Theta_H\) (\(\Theta_D\)). However, the experimental configuration used in TPD experiments (measuring background chamber pressure) precludes the direct observation of atomic desorption. Indirect isotope scrambling experiments suggest that some atomic desorption may also occur.\(^{12}\) The residence time of the monomer on the surface is estimated from DFT calculations\(^5\) to be only \(\sim 6\) min due to atomic desorption at \(T_p \approx 300\) K, and significantly less at higher \(T_p\). Certainly at \(T_p \approx 200\) K, STM observes that some monomer H is also produced at low \(\Theta_H\) but that it disappears in thermal annealing.\(^6\) There is, however, no direct evidence for atomic desorption at higher \(\Theta_H\) (\(\Theta_D\)) from the larger clusters. Atomic desorption is of great interest since state of the art “first principles” calculations of the time reversed process of atomic adsorption have recently been reported,\(^{13,14}\) and the atomic desorption should be related to the atomic adsorption through detailed balance.

In this paper, we report direct measurements of atomic D and molecular D\(_2\) desorbed from C(0001) as the result of a laser induced T-jump of the C(0001) surface to temperature \(T_p\) at various initial chemisorbed \(\Theta_H\), and especially at saturation coverage. These experiments measure the desorption of both species induced by the T-jump via \((2+1)\) resonantly enhanced multiphoton ionization (REMPI) using a tunable pulsed UV laser. The TOF distributions of the desorbing atoms and molecules are measured by varying the time delay between the REMPI laser and the T-jump laser, and this determines the energy distribution of the desorbing flux \(D_s(E,T_p)\) of each species. Using detailed balance, the atomic adsorption \(\Sigma(E,T_p)\) is obtained from \(D_s(E,T_p)\) for D atoms and compared with the theoretical adsorption calculations mentioned above.

II. EXPERIMENTAL

All experiments are carried out in a stainless steel ultra-high vacuum (UHV) chamber with a base pressure of \(\sim 10^{-10}\) torr that has been described in detail previously.\(^{11}\) Briefly, the chamber contains a resistively heated tungsten tube atom source for generation of thermal H (D) atoms (MBE-components), a differentially pumped quadrupole mass spectrometer for measuring TPD from the surface, a differentially pumped rotatable quadrupole mass spectrometer for measuring the TOF of laser desorbed molecules and a TOF ion detector to measure laser desorbed atoms and molecules via REMPI. A ZYA grade highly ordered pyrolytic graphite (HOPG) sample is glued to a tantalum disk that can be heated by electron bombardment on its back face. Combined with water cooling, the HOPG temperature range is 290–1400 K as measured by a C-type thermocouple placed between the HOPG back face and the tantalum disk. Before introduction into the UHV chamber, the HOPG sample is repeatedly peeled using adhesive tape until a visually flat surface is obtained. Following bake out, the sample is annealed to 1350 K for several minutes so that a clean surface is obtained with minimal defects. The sample surface quality is repeatedly monitored via TPD from the HOPG of H\(_2\) (D\(_2\)) and hydrocarbon fragments at saturation \(\Theta_H\) (\(\Theta_D\)) as these are sensitive to the presence of defects such as step edges.\(^{15}\)

The H (D) source generates atomic beams with thermal energies between 1800 and 2200 K and H(D) fluxes from \(10^{-3}\) to \(2 \times 10^{-2}\) ML s\(^{-1}\), (1 ML = \(3.8 \times 10^{15}\) cm\(^{-2}\)) depending on the H\(_2\) (D\(_2\)) pressure in the tube of the doser. The background pressure in the UHV chamber is typically \(P = 1.5 \times 10^{-5}\) torr during dosing. For most of the experiments reported here, the source temperature is 2200 K. The HOPG surface is 18 cm from the doser and is exposed for a specified amount of time to create a H or D coverage \(\Theta_H\) (\(\Theta_D\)). The saturation coverage is \(\Theta_H (\Theta_D) = 0.4\).\(^9\) A fresh dose of D or H atoms is used for each REMPI experiment. No measurable isotope effect is observed in either the atomic or molecular desorptions. Therefore, we only present results for D and D\(_2\) desorption because this isotope gives somewhat better signal/noise in experiments due to lower backgrounds and better energy resolution in the ion TOF.

A pulsed Nd:YAG-laser at 1064 nm incident on the surface at \(\sim 45^\circ\) from the surface normal creates a T-jump at the surface and induces all adsorbate chemistry: D desorption, D\(_2\) associative desorption, and diffusion/annealing of the surface. The output of the IR laser is apertured in the near field region of the laser and this aperture is optically imaged onto the surface thereby creating a nearly top hat (approximately constant laser intensity) spot on the surface of \(\sim 2.3\) mm\(^2\) area. The 10 Hz laser has a 16.5 ns pulse width. The T-jump of the HOPG surface induced by the laser irradiation is calculated by solving the coupled differential equations describing the time resolved heat formation and propagation via a three dimensional spatial finite element and time resolved model.\(^{16}\) This modeling shows that the surface temperature reaches its peak with a small delay relative to the laser pulse of \(\sim 12\) ns and that its duration is \(\sim 50\) ns. The optical absorption depth is only \(\sim 40\) nm, so only the near surface region is appreciably heated. The magnitude of the peak surface temperature in the T-jump \(T_p\) depends on laser intensity and is thus readily controlled during the experiments. \(T_p\) is given by the model as \(T_p = 290\) K + 7.4F\(_w\) where F\(_w\) is the laser fluence in mJ/cm\(^2\). The first term describes the rest temperature of the surface and the second the laser induced T-jump. The only significant uncertainty in this model is the value of the thermal conductivity between graphite planes,
and associative desorption, are described in terms of simple diffusion, atomic desorption, and molecular associative desorption, respectively. All chemical processes, i.e., diffusion, atomic desorption, and sorption, and molecular associative desorption, respectively. Desorption yields are measured by the REMPI intensity at the peak of the time of the flight distribution \( t_n \) and as a function of the number of prior laser shots. Desorbed species/inner states are as identified in the legend.

which appears to be sample dependent since there is some variability in the literature. This confers an uncertainty in \( T_p \) of \( \sim 200 \) K (at high laser fluence). Indirect experimental measurements of \( T_p \) via the temperature of the Maxwell–Boltzmann velocity distribution describing hydrocarbon fragments desorbed from a defected surface are in good agreement with this model.\(^\text{16}\) However, it should be emphasized that none of the details of the processes described in this paper depend on an accurate knowledge of \( T_p \). Typically, laser fluences \( F_o \leq 150 \text{ mJ/cm}^2 \) were utilized for the T-jumps and at this fluence there was no irreversible defect formation at the surface as monitored by subsequent TPD of adsorbed H. At higher fluences, however, TPD of adsorbed H did indicate some surface defect formation. These defects were easily removed by a slow anneal to 1350 K.

The chemistry induced by this T-jump is similar to the conventional thermally induced chemistry observed in TPD, but with an ultrafast temperature ramp of \( 10^{10}–10^{12} \) K/s. All chemical processes, i.e., diffusion, atomic desorption, and associative desorption, are described in terms of simple first order thermal kinetics, with rate constants given by \( k_i = v_i \exp(-V_i/k_B T) \), where \( i = d, a, m \) for diffusion, atomic desorption, and molecular associative desorption, respectively. \( v_i \) is the pre-exponential for the rate and \( V_i \) is the barrier for the process. Because the temperature dependences for all processes are dominated by the exponential terms, most of the chemistry occurs at or near the peak temperature, and when yields for the chemistry per laser pulse are small, the chemistry is well approximated as an isothermal processes at \( T_p \). Repeated laser shots at a given surface spot ultimately bleach the signal due to inducing \( D_2 \) (and D) desorption. By monitoring the bleaching curve, the number of desorbed molecules per laser shot is estimated. For the laser intensities used in the experiments reported here, desorption yields are quite small, typically \(<0.02 \text{ ML/pulse} \) (see Fig. 1). After bleaching one laser spot area, the sample is moved parallel to its surface to expose another irradiation area that does not overlap with the previous one. Seven different spots are irradiated on the HOPG in this way and desorption results averaged. In addition, TOF results represent averages over several independent D exposures on the surface because of the low signal to noise in these experiments.

2 + 1 REMPI of D and \( \text{D}_2 \) detect the atomic and molecular components, respectively, in the desorption flux generated via the T-jump of \( \text{C}(0001) \) surfaces with \( \text{D}_2 \) coverage. In contrast with the majority of previously reported REMPI experiments utilizing the \( S_1 \rightarrow 2S_{1/2} \) atomic two-photon transition,\(^\text{18}\) we use the slightly weaker \( S_1 \rightarrow 3S_{1/2} \) two-photon resonance (ca. 205 nm) as the resonant two-photon step in the REMPI of the atoms. This choice allows us to switch the REMPI detection scheme between atoms and molecules without change of the laser dye and any serious modifications in the nonlinear frequency doubling and mixing sections of the laser system. State resolved detection of desorbed \( \text{D}_2(v, J) \) is also observed using \( 2 + 1 \) REMPI transitions via the \( (X^1\Sigma^+_g \rightarrow E, F \Sigma^+_g) \) electronic band as the resonant two-photon step.\(^\text{19}\) We use the \( \Delta v=0, \Delta J=0 \) transitions in \( (X^1\Sigma^+_g \rightarrow E, F \Sigma^+_g) \) so that all rotational states with \( J<15 \) for both vibrational states can be detected without major changes in the laser system. Most molecular experiments reported here measured the \( v=0, J=2 \) and \( v=1, J=2 \) states of \( \text{D}_2 \). Only \( \text{D}_2 \) was probed via REMPI since there is a significant background of \( \text{H}_2 \) in the UHV chamber. We have, however, shown previously that there is no measurable isotope effect in the internal state averaged associative desorption.\(^\text{11}\)

The UV laser used for the REMPI (202–210 nm) is produced by frequency tripling a commercial Nd:YAG pumped dye laser in the range 606–630 nm (Continuum ND6000). The resulting UV is \( \sim 5 \) ns duration pulses with 0.35–0.5 mJ fluence and with 0.1–0.2 cm\(^{-1}\) spectral width. The UV laser beam is focused inside the UHV chamber to a \( \sim 0.1 \) mm diameter beam waist parallel to the sample surface and positioned at distance \( l \) from the surface. The UV laser is aligned to the center of the T-jump laser spot on the surface by translating it parallel to the surface while monitoring the REMPI intensity from D or \( \text{D}_2 \) desorbed by the T-jump. The distance between the UV laser focus and the sample surface \( l \) is set by accurately translating the UV laser beam normal to the surface from the point where it strikes the surface. Overall alignment uncertainty in \( l \) is estimated as 0.1 mm. Most experiments use \( l=2.9 \) mm. In the T-jump, desorption occurs over a time that is much smaller than the flight time of atoms or molecules to the focus of the UV laser. The two pulsed lasers are synchronized by external trigger electronics and TOF techniques can be used to measure the translational energy distributions of the desorbing species by measuring the REMPI intensity as a function of the delay between the REMPI laser and the T-jump laser. The REMPI intensity for the various desorbed species is measured by the ion signal on a microsphere channel plate at the end of a TOF tube, where the flight time selects the appropriate mass of the ionized species. Data acquisition is with a digital storage oscilloscope (LeCroy WaveSurfer 452 500 MHz 2 GS/s) which allows detection of the REMPI intensity for each laser.
T-jump and REMPI laser pair. Postaveraging in any appropriate manner is done subsequently in a computer. The principal uncertainty in the TOF (and hence in the energy resolution) is uncertainty in \( l \) which limits the TOF to \( \sim 3\% \) accuracy and energy resolution to \( \sim 6\% \).

The REMPI intensity \( I_i \) for either the atoms or molecules desorbed in the T-jump is proportional to the \( i \)th state-resolved desorption density \( D_{ni}(i,t) \), i.e., \( I_i(t) \propto D_{ni}(i,t)I_{uv} \), where \( I_{uv} \) is the UV laser intensity. It is assumed that the last photoionization step is fully saturated because of the high laser spectral density and tight laser focus.\(^{19}\) With the laser wavelength selected to probe either atoms or a fixed \( v, J \) state of \( \text{D}_2 \), translational energy distributions normal to the surface \( (E) \) are obtained by measuring the TOF from the surface to the focused UV laser beam by varying the delay \( t \) between the pulsed UV laser and the IR pulsed laser inducing the T-jump and desorption. The small time lag between the desorption peak and the T-jump laser (ca. 12 ns) is minimal compared to typical flight times of \( \sim 600 \) ns. Desorption fluxes at surface temperature \( T_p \) are obtained from the TOF signals in the usual manner via Eq. (1), where \( m_i \) is the mass of the \( i \) desorbing species,

\[
D_i(i,E,T_p) = \tau^2 D_{ni}(i,t,T_p) \quad \text{and} \quad E = \frac{1}{2} m_i \left( \frac{l}{t} \right)^2 .
\]

Using detailed balance, the desorption flux can be converted to the time reversed process of sticking \( S(i,E,T_p) \) for comparison with theoretical calculations via Eq. (2).

\[
D_j(i,E,T_p) \propto E \exp(-E/k_BT_p)\exp(-E_i/k_BT_p)S(i,E,T_p) ,
\]

where \( E_i \) is the internal energy of the \( i \)th state. For atom desorption, \( E_i = 0 \).

No attempt was made to accurately compare relative \( D_{ni}(i,t) \) for the various \( i \) species; D atoms, \( \text{D}_2(v=0) \) and \( \text{D}_2(v=1) \) because the wavelength changes necessary to detect the various species caused significant optical realignment of the REMPI excitation system. We note, however, that REMPI intensities for \( \text{D}_2(v=0) > \text{D}_2(v=1) \approx \text{D} \). The D atom desorption flux is estimated by comparing the REMPI intensity from laser induced desorption to that of the D atom beam source used in the dosing since this density is roughly known. The total \( \text{D}_2 \) and D desorption flux integrated over the bleaching is known from the coverage. This indicates that associative desorption is the dominate desorption mechanism.

III. EXPERIMENTAL RESULTS

Both D and \( \text{D}_2 \) are observed by \( 2 + 1 \) REMPI following a laser induced T-jump to \( \sim 1200 \) K of the HOPG with \( \Theta_D \) at saturation. Both \( v=0, J \) and \( v=1, J \) \( \text{D}_2 \) are easily observed. All species show characteristic TOF distributions (as described later) and the density of desorbed D and \( \text{D}_2 \) are taken to be proportional to the REMPI intensity of the respective peaks of the TOF distributions \( t_m \) since the TOF distributions are nearly independent of \( F_{uv} \). As shown in Fig. 1, the desorption of both species bleaches with repeated laser shots due to desorption of \( \text{D}_2 \) and D from the irradiated spot and the lowering of \( \Theta_D \) in the chemisorbed state for subsequent laser shots and due to thermal annealing of the chemisorbed state. The D desorption show a rapid initial bleaching, followed by a slower bleaching at the same rate as that for the molecules. The atomic bleaching rate is approximately represented as the sum of two exponentials, loosely defining an initial rate of bleaching \( R_i \) and a later rate of bleaching which is also characteristic for the molecular bleaching and therefore labeled \( R_m \). Previous experiments measuring internal state averaged \( \text{D}_2 \) associative desorption induced by a laser T-jump also showed bleaching and demonstrated that diffusion into the bleached spot from adjoining areas did not occur during the sequence of laser shots.\(^ {11} \) Figure 1 suggests that atoms from two types of clusters are desorbed during the sequence of laser shots. Since the initial desorption must represent the most weakly bound D, desorption characterized by \( R_i \) is identified as D desorption from less stable cluster configurations with weakly bound D, while the desorption characterized by \( R_m \) originates from more stable cluster configurations with more strongly bound D.

Thermally annealing a freshly prepared surface with \( \Theta_D \) at saturation to 510 K for 1 min prior to laser induced desorption exhibits only the slow bleaching curve characterized by \( R_m \) and with roughly the same intensity as for the sample that has been subjected only to the prior laser shots. This suggests that several prior laser T-jumps is equivalent to a slow thermal anneal. Presumably, the thermal or laser T-jump anneal desorbs D from less stable D sites and simultaneously converts the D clusters to the most stable configurations via D atom diffusion, as well as inducing simultaneous \( \text{D}_2 \) associative desorption. Note that this interpretation also implies that \( \text{D}_2 \) associative desorption occurs principally from para dimer configurations in the most stable larger clusters, just as for the dimers.\(^ {5} \) From the approximate estimates of the various detected desorption fluxes discussed earlier, we estimate that the atomic desorption integrated over the laser induced bleaching accounts for \( \sim 5\% \) of the total desorption. This estimate is used to scale the D to \( \text{D}_2 \) desorption intensities in Fig. 1 and implies that initial desorption from the metastable large clusters is dominated by atomic desorption, but that after some thermal annealing to the more stable cluster configurations, molecular associative desorption dominates the desorption process.

Figure 2 shows bleaching curves for D desorption for a T-jump to \( T_p \sim 1500 \) K for different initial \( \Theta_D \) as indicated in the figure. \( \Theta_D \) is estimated in this figure by assuming a saturation coverage of 0.4 for \( \sim 8 \) ML D exposure and using relative TPD intensities of \( \text{D}_2 \) associative desorption to scale \( \Theta_D \) for lower D exposures. This figure shows (1) that the flux of D desorption for the first few laser shots is nearly independent of \( \Theta_D \) while it is proportional to \( \Theta_D \) for the later shots, (2) that \( R_i \) decreases with \( \Theta_D \), and (3) that \( R_m \) is nearly independent of \( \Theta_D \). Following the interpretation suggested for Fig. 1, this implies that upon initial exposure to the D atom beam (low \( \Theta_D \)), principally small cluster configurations are produced (due to limited D diffusion) with many low stability D sites. As \( \Theta_D \) increases and the cluster size grows,
both the number of unstable and stable D sites (perhaps produced principally via thermal annealing of less stable sites via prior laser shots) in the clusters increase.

As described previously, the TOF density distribution of atoms and molecules desorbed from the surface are obtained by varying the delay between the REMPI laser and the T-jump laser. This is converted to $D_f(i, E, T_p)$ via Eq. (1) and subsequently to $S(i, E, T_s)$ via Eq. (2). Because the flight distance from the surface to the REMPI laser ionization volume is small (typically $\sim 2.9$ mm), it is important to ensure that it is determined accurately (to $\sim 0.1$ mm) to give an accurate transformation between $t$ and $E$ in Eq. (1). Figure 3 shows $D_f(i, E, T_p)$ for $v=0$, $j=2$ and $v=1$, $j=2$ D$_2$ from associative desorption from REMPI following a T-jump to $T_p \sim 1400$ K compared to that obtained previously via laser assisted associative desorption into the differentially pumped rotating mass spectrometer. The latter has a TOF distance $l \approx 10$ cm in which there was little absolute error. The good agreement between the $D_f(i, E, T_p)$ for D$_2$ obtained with REMPI to the previous experiments demonstrates that $l$ is accurately determined in the REMPI experiments. Note that the high $E$ side of $D_f(i, E, T_p)$ is reduced by $~0.3$ eV in $v = 1$ relative to that of $v = 0$. This appears to be slightly less than the D$_2$ vibrational frequency of 0.37 eV.

Because the D atom desorption seems to occur in two distinct groups during repeated laser shots due to the nearly biexponential bleaching dependence (see Figs. 1 and 2), the TOF spectra have been obtained separately for the two groups. The D atom TOF corresponding to $\Theta_d = 1200$ K shows these results averaged over first 20 laser shots and $S(i, E, T_s)$ from the D atom TOF for the second 80 laser shots. Figure 4(a) shows $D_f(i, E, T_p)$ obtained from the D atom TOF for the two fractions following a T-jump to $T_p \sim 1200$ K and Fig. 4(b) shows these results converted to $S(i, E, T_s)$ via detailed balance. Note that the
second fraction following \( R_m \) bleaching has a tail to a slightly lower \( E \) in \( D_f(i, E, T) \) and consequently also in \( S(i, E, T) \) relative to the initial fraction with \( R_i \) bleaching. The low signal/noise in this plot is due to a substantial variation in shot to shot D atom desorption flux due to UV laser intensity fluctuations, T-jump laser intensity fluctuations, variations in the laser irradiation spot, and in the D atom dosing. Random averaging the desorption at each \( r \) over each possible variable ensured that the true TOF was obtained without experimental artifact.

**IV. DFT CALCULATIONS**

The DFT calculations were performed with the plane wave based DACAPO program package, applying ultrasoft pseudopotentials to describe electron-ion interactions, and the Perdew–Wang functional (PW91) (Ref. 22) for the electronic exchange correlation effects. The electron wave functions and augmented electron density were expanded in plane waves with cutoff energies of 25 and 140 Ry, respectively. The Chadi–Cohen scheme with six special points was used for sampling of the surface Brillouin zone. The graphite surface was modeled with rhombohedral, periodically repeated slabs consisting of one graphite sheet with 72 carbon atoms, and separated by 15 Å of vacuum. The potential energy curves for diffusion of H atoms on graphite surfaces were calculated applying the nudged elastic band method. Details of the DFT calculations will be presented elsewhere.

Figure 5 shows a large variety of 4H (or 4D) atom clusters considered in the DFT. Also shown at the side of Fig. 5 are the DFT energies of the cluster configurations relative to the most stable cluster configuration \( \Delta E_j \), where \( j \) refers to the cluster label in Fig. 5. There is obviously a wide distribution of cluster stabilities, which for the purposes of later discussion we simply break into three classes: stable clusters (\( \Delta E_j < 0.6 \) eV), moderately stable clusters (0.6 eV < \( \Delta E_j < 1.2 \) eV), and unstable clusters (\( \Delta E_j > 1.2 \) eV). Calculations on 5H atom and 6H atom clusters also show a similar wide distribution of cluster stabilities and will be reported separately. Therefore, we take the 4H clusters as qualitatively representative for all of the complex and possibly larger clusters present in C(0001) with large \( \Theta_H \). We also note that there should be no isotopic difference in any of the cluster energies, and only miniscule isotopic zero point energy differences for any of the barriers \( V_a \) describing the chemical processes. Therefore, theoretical chemical processes on D covered C(0001) are essentially identical to those from the DFT calculations on H covered C(0001) so that the H or D labels are used interchangeably.

The barriers to H atom desorption from the various clusters are estimated simply as the energy of the desorption process, \( V_a \approx E_i(3H) + E_{l(H)}(g) - E_l(4H) \), where \( E_l(4H) \) is the energy of formation of the \( l \) four atom H cluster, \( E_i(3H) \) is the energy of formation of the \( l \) three atom H cluster left on the surface by desorption of the least stably bound H atom and \( E_{l(H)}(g) \) is the energy of formation of the H atom in the gas phase. Direct DFT calculations of barriers to H atom addition \( V_H^{l+} \) for 2H and 3H clusters suggest that desorption barriers estimated via this method are accurate for the stable clusters, but may underestimate the full barrier by <0.2 eV for the less stable clusters. Since these corrections are quite small relative to the variation of \( V_a \) with cluster configuration \( j \), we do not attempt to correct \( V_a \) for the small barrier to H addition from the gas phase. A plot of the barriers \( V_a \) versus \( \Delta E_j \) is given in Fig. 6 and clearly demonstrates an approximate inverse linear relationship between \( V_a \) and \( \Delta E_j \). The points given by the triangles correspond to the case where atomic
The D dosing and all subsequent T-jump experiments have been performed at a resting surface temperature $T_r = 290$ K. There may be some initial preferential formation of more stable clusters at very low $\Theta_2$, due to the lower barrier to D atom adsorption in these clusters, but extended exposure to the D beam should produce nearly all possible clusters and cluster configurations. While careful monitoring of the time scale during the experiments was not recorded, T-jump experiments were not initiated until typically 10 min after H exposure by the atom source and continued for typically 5 min longer. Assuming normal pre-exponential factors ($\sim 10^{13}$ s$^{-1}$) for all kinetics (diffusion, atom desorption), this time scale implies that all cluster structures with barriers $V_i \leq 0.9$ eV will not be probed during the subsequent T-jump experiments. From Fig. 6, this means that most if not all of the unstable clusters will no longer exist during the T-jump experiments since they will have already transformed into more stable structures on C(0001) by D atom diffusion or atomic desorption. During typical T-jump experiments, the surface transiently reaches $T_p \approx 300$ K, causing both desorption of D and D$_2$, as well as extensive annealing via D atom diffusion of the remaining cluster structures to the most stable cluster configurations. As Fig. 6 demonstrates, $V_a$ is inversely related to the stability of the clusters configurations. Thus, the moderately stable cluster configurations exhibit the fastest atomic desorption rate and therefore dominate the initial $R_i$ fraction. As the moderately stable clusters anneal by repeated T-jumps, only atomic desorption from the most stable clusters is possible and it is these which dominate atomic desorption described by the $R_m$ fraction. Figure 7(a) illustrates the competition between thermal annealing of unstable clusters by diffusion with atomic desorption in the DFT calculations. Annealing generally wins in TPD because of the lower barriers to diffusion relative to atomic desorption from these clusters. However, for the fast T-jump to very high temperatures, both processes are substantial.

Figure 7(b) indicates that it is unlikely for unstably bound atoms to diffuse away from the unstable clusters, i.e., for the clusters to disproportionate. H atom desorption barriers along the disproportionation path are generally less than diffusion barriers so that the atom generally desorbs before it can escape via diffusion.

For atomic desorption, $D_i(i,E,T_p)$ is converted to $S(i,E,T_p)$ via detailed balance, Eq. (2), in order to compare with dynamical calculations of atom sticking on C(0001). Figure 4 separates the two desorbing fractions, i.e., those following $R_i$ bleaching (moderately stable clusters) and those following $R_m$ bleaching (stable clusters). For both groups, there is an initial increase in $S$ with $E$ followed by a decrease at higher $E$. The initial increase with $E$ is most pronounced for the moderately stable clusters ($R_i$ bleaching) since $S$ for the stable clusters ($R_m$ bleaching) tails to lower $E$. This implies that the stable clusters have slightly lower barriers to atomic desorption than moderately stable ones. This has previously been observed in DFT calculations for 2 and 3 atom clusters.

Kerwin and Jackson performed state of the art “first principles” calculations of the sticking of H (D) on C(0001) based on classical dynamics on a DFT based PES. This

V. DISCUSSION

While the cluster configurations considered in Fig. 5 are not exhaustive, it is apparent that most of the stable clusters contain predominately ortho-H configurations. Stable 5H and 6H clusters also show a preponderance of ortho-H configurations. This observation is in good agreement with angle resolved x-ray absorption experiments which demonstrate that the ortho configuration dominates at high $\Theta_H$ on C(0001).
PES includes direct coupling to lattice coordinates describing the puckering of the C out of the plane that is necessary for the H (D) to form a bond to the graphite. Dissipation of energy from the nascent energy rich C–H bond to the rest of the graphite lattice, a necessary condition for sticking, is included by coupling the local DFT PES to a large cluster of graphite atom lattice vibrations. On the bare surface, a threshold in $S$ is observed at the atomic adsorption barrier $V_{th}$ (or $V_p$) (0.24 in their calculations), followed by a steep increase in $S$ peaking at $\sim 0.5 \ eV$ and then a decrease. The decrease in $S$ with $E$ is due to the increasing difficulty in dissipating the excess energy in the nascent C–H(D) bond. When this excess energy is not fully dissipated within a few C–H(D) vibrational periods, the H(D) does not remain bound to the C(0001). Because barriers for sticking of additional H(D) to an already adsorbed H(D) are often smaller than the initial barrier for a single H(D) adsorption, Kerwin and Jackson have also shown via related model PES that as $V_{th}$ decreases, the entire $S$ peak shifts to lower $E$. We anticipate that addition of D to existing clusters will exhibit a range of low thresholds to higher energies, the entire peak shifting to higher $E$. We anticipate that local trans-configurations of Fig. 5 have not been calculated via DFT. The associative desorption barriers are much greater than that predicted via DFT. We certainly anticipate that local trans-configurations in the larger clusters will dominate associative desorption from these as well. All of these clusters are in the most stable category. 

The translational energy normal to the surface $E$ released in associative desorption at the surface temperature $T_p$ is given as

$$E = V_{D_2} + (E_{th})_{p} + \frac{1}{2}k_BT_p - E_i - e_i - e_s,$$

where $V_{D_2}$ is the barrier to dissociation of $D_2$ from the gas phase to form a given cluster configuration, $(E_{th})_{p}$ is the thermal energy in the transition state in modes perpendicular to the reaction coordinate at surface temperature $T_p$, $(1/2)k_BT_p$ is the thermal energy along the reaction coordinate, $E_i$ is the translational energy parallel to the surface, $e_i$ is the internal energy of state $i$ of $D_2$, and $e_s$ is the energy loss to the C(0001) surface during associative desorption. Note that $E_i \sim 0$ due to the peaking nearly normal to the surface in the angular distribution of $D_2(E,T_p)$. The thermal energy at the transition state added to $V_{D_2}$ is modest ($< 0.3 \ eV$). As shown in Fig. 3 and discussed earlier, $D_2(E,T_p)$ summed over all internal states produced in associative desorption is a very broad distribution in $E$ peaking at $\sim 1.3 \ eV$. It was previously unclear whether the moderate average translational energy (relative to the anticipated total available energy of $\sim 3.4 \ eV$) and very broad distribution were due to a wide distribution of internal states produced in the associative desorption, a wide distribution of lower $V_{D_2}$ from different clusters or due to a large $e_s$ and distribution in $e_s$. The state resolved measurements in Fig. 3 clearly demonstrate that the distribution of internal states produced in associative desorption is not the dominant loss and broadening mechanism. The barriers to associative desorption for the four clusters in Fig. 7(c) combined with the binding energies for the dimers remaining on the surface gives $(V_{D_2})_P = 2.5 \pm 0.35$. A similar $(V_{D_2})_P$ is obtained for associative desorption from a wide range of trans-clusters with four, five, and six atoms assuming an associative desorption barrier of $\sim 1.4 \ eV$ from all clusters. Thus, the observed $(E) \approx (E_{th})_{p} + (E_{th})_{D_2} + (E_{th})_D$ and the breadth of the observed distribution in $E$ are much greater than that predicted via DFT. The only significant term not included in this comparison is the energy loss to the surface, and this implies that the average energy lost to the surface, $(<e_s>) > 1 \ eV$ and that there is a broad distribution of such energy losses. This is consistent with the fact that the lattice distortion energy is $\sim 1 \ eV$ for a large dissociated D atom in the adsorbed state (for the dimers) and much of this is undoubtedly retained in the surface during associative desorption. Thus the response of the lattice to the release of the puckering configuration in associative desorption seems midway between an adiabatic and sudden response. 

As noted earlier, the shift in the high energy region of $D_2(v=0, J=2, E, T_p)$ relative to $D_2(v=1, J=2, E, T_p)$, $\Delta D_2v=0.3 \ eV$ implies a large vibrational efficacy $\eta_v = \Delta D_2v/\Delta e_v=(0.3/0.37)=0.8$. This is entirely consistent with the extended $D_2$ bond length in the transition state in the DFT calculations.

**VI. SUMMARY AND CONCLUSIONS**

REMPI detection shows that D atoms desorb directly into the gas phase following a laser induced T-jump of D chemisorbed on C(0001) at various initial coverages $\Theta_D$. Bleaching experiments with repeated laser T-jumps to peak temperature $T_p$ suggest that there are qualitatively two different classes of clusters since the bleaching is roughly biexponential, i.e., less stable ones with weakly bound D (fast initial bleaching $R_f$) and more stable ones with more strongly bound D (slower bleaching $R_m$). TOF experiments measure the energy resolved desorption flux $D_j(i,E,T_p)$ which is converted to energy dependent atomic sticking $S(i,E,T_p)$ by detailed balance. These experiments show that the more stable clusters have slightly lower barriers to atomic desorption than the less stable clusters, in agreement with DFT calculations. The atomic adsorption inferred from the experiments is in reasonable accord with first principles theoretical calculations of sticking. In addition, state resolved $D_2$ associative desorption is observed by REMPI using TOF techniques. The state resolved translational energy distributions are similar to those observed previously with internal state averaging. This result, when combined with DFT estimates
of the total energy released for the various clusters, implies that there is substantial energy loss to the surface in associative desorption and that the large broadening in the translational energy distributions is due to a wide distribution of energy losses to the surface. Shifts in the high energy threshold between $v=0$ and $v=1$ D$_2$ produced in the associative desorption suggest a high vibrational efficacy for the dissociative adsorption/associative desorption chemistry.

We report a variety of DFT calculations on 4H(D) clusters on C(0001) that not only support the qualitative interpretation of the experiments, but also provide much a more quantitative physical picture of the chemical processes induced by the T-jump. The calculations demonstrate that a wide variety of cluster stabilities $\Delta E_j$ exist, as well as a wide range of diffusion barriers $V_d$ between the different cluster configurations and barriers to atomic desorption $V_a$. Barriers to associative desorption from clusters containing trans-configurations are similar to those for dimer desorption. These calculations suggest that thermal annealing is a complex combination of atomic desorption, atomic diffusion to more stable cluster configurations, and associative desorption. The clusters are arbitrarily divided into three classes: unstable, moderately stable, and stable to connect with the experimental discussion. The unstable clusters are probably not observed in the experiments since atomic desorption/diffusion converts the clusters to moderately stable ones prior to the T-jump. The moderately stable clusters have the lowest $V_a$ and are desorbed most easily ($R_f$ fraction), while the most stable clusters have higher $V_a$ and are more difficult to desorb ($R_m$ fraction). $V_d$ between two cluster configurations always favors formation of the more stable configuration, so that repeated T-jumps will always anneal the clusters to the most stable ones.

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10 Z. Sljivancanin and B. Hammer (to be published).
12 T. Zecho (private communication).