Inelastic and Reactive Scattering Dynamics of Hyperthermal O and O₂ on Hot Vitreous Carbon Surfaces

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ABSTRACT: We have undertaken a series of experiments to learn the mechanisms of carbon oxidation over a wide range of temperatures that extend to the conditions encountered during atmospheric re-entry, with a particular interest in understanding how these mechanisms change with temperature. We report here the hyperthermal scattering dynamics of ground-state atomic oxygen, O(3P), and molecular oxygen, O₂(3Σg⁻), on vitreous carbon surfaces at temperatures from 600 to 2100 K. A molecular beam containing neutral O and O₂ in a mole ratio of 0.93:0.07 was prepared with a nominal velocity of 7760 m s⁻¹, corresponding to a translational energy of 481 kJ mol⁻¹ for atomic oxygen. This beam was directed at a vitreous carbon surface, and angular and translational energy distributions were obtained for inelastically and reactively scattered products with the use of a rotatable mass spectrometer detector. Unreacted oxygen atoms exited the surface through both impulsive scattering and thermal desorption. The preferred scattering process changed from impulsive scattering to thermal desorption as the surface temperature increased. O₂ scattered mainly impulsively from the surface, and its scattering dynamics were essentially unaffected by surface temperature. The predominant reactive product was carbon monoxide (CO). Carbon dioxide (CO₂) was also formed at lower surface temperatures. The flux of the CO product rose with temperature to a maximum at approximately 1500–1900 K, depending on heating rate, and then decreased with increasing surface temperature. The CO₂ flux dropped dramatically with increasing surface temperature and was below detectable limits above 1100 K. A minor reactive pathway was identified that produced O₂, presumably through a direct Eley–Rideal reaction of an incident oxygen atom with an O atom residing on the surface. Decreased oxygen surface coverage at higher temperatures was found to limit the reactivity of the surface by inhibiting the production of CO and CO₂ at very high surface temperatures. The observed inelastic and reactive scattering behavior reveals a complex interplay between reactivity and surface temperature.

I. INTRODUCTION

Space vehicles that enter the Earth’s atmosphere at hypersonic speeds require a thermal protection system (TPS) to shield the vehicle from high heat loads. In the re-entry environment, the boundary layer in contact with the hot surface consists of partially dissociated air, with N₂, O₂, and O being the dominant species for vehicles re-entering from low Earth orbit (LEO). These species collide with the TPS surface and may scatter without reaction back into the boundary layer. Atomic and molecular oxygen can also react to form volatile products that either scatter directly or desorb thermally into the boundary layer. The deposition of energy into the surface or the boundary layer depends critically on the details of the gas–surface interaction dynamics, which are largely unknown under such extreme conditions. A thorough understanding of these dynamics would enable more accurate modeling of thermal loads during atmospheric re-entry and therefore mitigate the need for overly conservative TPS designs. TPS materials for applications where shape change is undesirable are typically carbon–carbon composites that oxidize in air at high temperatures (>800 K) and are designed to ablate during the hypersonic flight period, where the surface may reach temperatures well above 2000 K. Vitreous carbon, also referred to as glassy carbon, can serve as an experimental model for such materials. This material has both a high melting point and high thermal conductivity, as well as a low coefficient of thermal expansion.¹ These characteristics have motivated its use as the matrix in carbon–carbon composites on vehicle nose-cones and leading edges in the past.¹

The structure of vitreous carbon has been subject to debate. It has been shown to consist largely of sp²-bonded carbon with fullerene structures.² However, neutron diffraction measurements have shown that fullerene structures are present only in trace amounts in vitreous carbon, suggesting instead that it consists of a graphite-like structure with short-range order.³ Additional studies have reported that vitreous carbon is composed of crystallites that consist of small, randomly oriented stacks of curved graphene sheets.⁴,⁵ The disordered orientation of the crystallites encloses small voids.⁶–⁸ Consequently, the density of vitreous carbon (1.42 g cm⁻³) is lower than that of pyrolytic graphite (2.25 g cm⁻³). Nevertheless, vitreous carbon is considered to be nonporous.
The oxidation of vitreous carbon by molecular oxygen revealed pores that had been initially closed to the atmosphere. X-ray photoelectron spectroscopy (XPS) studies have shown that O$_2$ dissociatively chemisorbs on vitreous carbon at edge carbon atoms, with the formation of single bonds between surface carbon atoms and adsorbed O atoms, possibly in an epoxide formation over carbon bridges. Additional temperature-programmed desorption (TPD) studies found that the production of CO and CO$_2$ in the temperature range of 723–873 K corresponded to the decomposition of carboxylate and ether-like species on the surface. Vitreous carbon etching by atomic oxygen was observed upon exposure to suprathermal O atoms at 299 K. The probability of a carbon atom being removed by a suprathermal O atom from vitreous carbon was $2.1 \times 1.2 \times 10^{-2}$. This probability is nearly twice as high as the value for pyrolytic graphite, which was found to be $1.3 \times 10^{-2}$. This indicates that vitreous carbon is the more reactive substance. This enhanced reactivity is presumably the result of the porous structure of vitreous carbon.

Highly oriented pyrolytic graphite (HOPG) has often been used as a model surface for investigating the degradation of carbon-based materials. HOPG is composed of graphene crystallites that are microns to tens of microns in length and oriented along the basal plane, with their c axes being parallel to the surface normal of the overall crystal. In the oxidation of HOPG, it can be helpful in the understanding of O and O$_2$ reactions on vitreous carbon, as both these sp$^2$ allotropes of carbon may undergo oxidation and etching through similar mechanisms, albeit with different rates. The oxidation of HOPG has been studied extensively in environments relevant to LEO, where the dominant chemical species are O atoms that can collide with the ram surfaces of orbiting spacecraft with high relative velocities corresponding to O atoms with $\sim$500 kJ mol$^{-1}$ striking the surfaces. Laboratory experiments of these hyperthermal O-atom interactions, such as the experiment described in this article, typically expose surfaces to O$_2$ as well as O. Nevertheless, O$_2$ is only weakly reactive with HOPG and probably also with vitreous carbon. O$_2$ can physisorb on a pristine graphite surface, but it is bound by a low barrier of $\sim$0.1 eV. Furthermore, O$_2$ has a low sticking coefficient: $1.53 \pm 0.35 \times 10^{-10}$ on pristine surfaces, increasing to $10^{-10}$ on defect sites. The reaction of O$_2$ with HOPG occurs mainly through dissociative chemisorption, which follows a low-barrier path only when O$_2$ binds at defect sites. However, the low defect density of an HOPG surface ($3-4 \, \mu m^2$) keeps the overall reactivity with O$_2$ low. Even at hyperthermal incidence energies, O$_2$ would be expected to scatter inelastically with high probability and not contribute significantly to the removal of carbon. In contrast, the reactivity of hyperthermal O atoms is high and extends beyond defect sites. Postexposure characterization of room-temperature HOPG subjected to hyperthermal O and O$_2$ bombardment revealed that C$\cdash$O, C=O, or O$\cdash$C=O and O$\cdash$C=O functional groups populated the surface. In the same study, scanning tunneling microscopy studies showed that the surface became rough and formed hillock-like structures. Nicholson, Minton, and Sibener conducted a series of experiments that studied the chemical reactivity of HOPG in the range of 300–500 K when exposed to higher fluxes of hyperthermal O atoms. They observed the etching of HOPG, and they found that the reaction probability nearly tripled—from one C atom removed for every 22 incident O atoms to one C atom removed for every 8 incident O atoms—when the surface temperature was increased from 298 to 493 K. In addition, they observed the formation of shallow circular etch pits that grew in diameter with increasing oxygen atom fluence, indicating that O atoms reacted preferentially with carbon atoms at the edges of the graphene planes, most likely through thermal mechanisms—i.e., in thermal equilibrium with the surface. At elevated temperatures of $\sim$773 K and above, the circular etch pits did not form, and the surface became randomly rough, presumably through the coalescence of individual etch pits. Molecular beam scattering studies that utilized a beam containing hyperthermal O atoms were conducted in an attempt to probe the details of the mechanisms that lead to the removal of carbon from HOPG. CO and CO$_2$ products were observed from an HOPG surface at 503 K, and they exited the surface with similar yields via thermal and nonthermal mechanisms.

Theoretical studies have shown that the gasification of carbon by O atoms occurs mainly at specific reactive sites involving semiquinone or lactone functional groups, which form at defect sites during O atom bombardment. When pristine HOPG is exposed to hyperthermal O atoms, the incident O atoms add to carbon bridges to form epoxide groups, with calculated adsorption energies in the range of 0.95–3.2 eV depending on the surface coverage and level of theory being used. These epoxide groups can migrate across the surface over low diffusion barriers, calculated to be in the range of 0.36–0.38 eV. The migration of epoxide groups to the vicinity of semiquinone or lactone sites promotes the formation of CO or CO$_2$ by decreasing the barrier to reaction. In addition, the excess oxygen surrounding a reactive site was found to lower the reaction endothermicity by saturating the remaining dangling bonds around carbon vacancies created during the reaction. Theoretical studies have found that the dominant reaction at an HOPG surface during hyperthermal O-atom bombardment is the abstraction of a surface-adsorbed O atom by an impinging oxygen atom to produce O$_2$ through a direct (Eley–Rideal) reaction. Reactions of this type do not lead directly to the removal of carbon, but they may limit the reaction rate by removing adsorbed O atoms, which would otherwise be available to facilitate the production of CO or CO$_2$. The theoretical studies have not identified an Eley–Rideal abstraction pathway through which CO or CO$_2$ might be formed.

Two noteworthy theoretical studies have investigated the effect of surface temperature on the interaction of hyperthermal O atoms with carbon surfaces. ReaxFF calculations by van Duin and co-workers probed the reaction dynamics of O atoms with HOPG. It was shown that an increase in the surface temperature resulted in a larger amount of carbon removed from the surface, although the fraction of the carbon atoms removed as CO or CO$_2$ as a function of temperature was not discussed. Morón et al. conducted calculations on O-atom collisions with a preoxidized HOPG surface with the use of a flexible periodic LEPS potential energy surface based on density functional theory. They found that inelastic scattering of O and a direct Eley–Rideal reaction of an incident O-atom with a surface-adsorbed O to form O$_2$ were the two main processes observed with surface temperatures of 100 and 900 K and with incident O-atom energies up to 2.0 eV. For unreacted O atoms, they observed direct scattering and thermal desorption, and they found that thermal O atom desorption processes became more significant at the higher temperatures with incidence.
energies in the range of 1–2 eV. The desorbing oxygen atoms resulted from weakly bound \( E_{\text{ads}} = 0.68 \text{ eV} \) adatoms on carbon bridges that were removed when an incident O atom from the gas phase adsorbed at a nearby site.\(^{34} \) They also reported the observation of some events where the inelastic scattering of an impinging atom induced the thermal desorption of a preadsorbed O atom at a nearby site, although such events were only significant at a high temperature of 1500 K. The theoretical studies by Morón et al. did not address the possible formation of CO or CO\(_2\).

Experiments conducted on surfaces at very high temperatures have only focused on the interaction of thermal O and O\(_2\) with graphite. Rosner and Allendorf studied the probability of thermal O and O\(_2\) reactions with a graphite filament at temperatures ranging from 1000 to 2000 K.\(^{35} \) The reaction did not follow Arrhenius behavior in the temperature range studied, as the reaction probability for carbon removal increased with temperature and reached a maximum at approximately 1600 K before decreasing as the temperature was increased further. Similar non-Arrhenius behavior was observed by Olander et al., who monitored the CO reaction product when HOPG was exposed to O\(_2\) over a similar temperature range.\(^{37} \) In addition to the non-Arrhenius behavior, they noted a hysteresis in the temperature dependence, where the reaction probabilities with decreasing temperatures over the same temperature range from 600 to 2100 K, with detailed dynamical scattering data collected for two widely spaced temperatures of 800 and 1875 K. Thus, the important temperature-dependent inelastic and reactive scattering dynamics have been ascertained and investigated in detail. The use of hyperthermal O and O\(_2\) provides for a highly localized interaction at the surface,\(^{38} \) which can reveal details about surface changes at the atomic level during oxidation. In addition, hyperthermal incident species allow for a clear distinction between nonthermal and thermal processes at the surface, as products of processes that occur in thermal equilibrium with the surface will desorb with much slower velocities than products that exit the surface nonthermally after a hyperthermal impact. Furthermore, the relative importance of thermal vs nonthermal processes found with hyperthermal incident species may reveal whether surface temperature or incidence energy has the stronger influence on the oxidation reactions at the surface. From the detailed dynamical data that have been obtained combined with information gleaned from relevant studies in the literature, the essential mechanisms of the high-temperature oxidation of vitreous carbon have been inferred and are presented below.

II. EXPERIMENTAL METHODS

The experiments were performed with the use of a crossed molecular beams apparatus reconfigured for surface scattering.\(^{39} \) Brieﬂy, a pulsed beam containing high-translational-energy (or “hyperthermal”) O and O\(_2\) was directed at a heated vitreous carbon surface (Figure 1a). Volatile reaction products were monitored with a mass spectrometer that rotated about the same axis as the surface in the plane defined by the surface normal and the beam. Products were detected at a variety of final scattering angles, \( \theta_0 \) for two angles of incidence, \( \theta_i = 45^\circ \) and 60\(^{\circ} \). All angles are in the same plane and referenced to the surface normal, with positive final angles being on the opposite side of the surface normal from the incidence angles. Products that entered the detector were ionized in an electron-impact ionizer,\(^{37} \) filtered with a quadrupole, and detected with a Daly type ion detector\(^{45} \) in a pulse-counting mode. The ion pulses were accumulated by a multichannel scaler. The distributions collected with the multichannel scaler are number density distributions of scattered products as a function of their flight times over the 33.7 cm distance from the surface to the electron-impact ionizer. These \( N(t) \) distributions are commonly called time-of-flight (TOF) distributions. Translational energy distributions, \( P(E_T) \), of the scattered products, which are proportional to flux, are derived from the TOF distributions with the use of a simple density-to-flux conversion that assumes a monoenergetic incident beam.\(^{40,44} \) When total relative flux is
had an average translational energy of 481.6 kJ mol$^{-1}$ and a translational energy of 962.4 kJ mol$^{-1}$. The detector was triply diluted with a base pressure of <10$^{-11}$ Torr that did not rise during data collection.

The laser-detonation source used to generate hyperthermal O and O$_2$ is based on an original design by Physical Sciences, Inc.$^{46}$ Translational energy distributions and component fluxes of the hyperthermal beam were obtained by lowering the sample out of the beam path and directing the beam into the detector. The beam passed through a 2.0 mm diameter skimmer that was 77 cm from the nozzle orifice. The beam was further collimated by a 1.3 mm diameter aperture that was 3.54 cm from the skimmer. The sample surface was 97.75 cm from the nozzle orifice. The source was operated at a repetition rate of 2 Hz. A synchronized chopper wheel, with three equally spaced slots of 1.5 mm width and a rotation rate of 300 Hz, was used to select a narrow distribution of velocities from the beam. The beam was composed of 93% O(3$^3$P)$^{37}$ and had an average translational energy of 481.6 kJ mol$^{-1}$ and an energy width (full width at half-maximum) of 55 kJ mol$^{-1}$ (Figure 2). The remainder of the beam was O$_2$(3$^3$Σ$^−$)$^{48}$ and had a translational energy of 962.4 kJ mol$^{-1}$ and an energy width of 160 kJ mol$^{-1}$.

![Figure 2. Translational energy distributions of the energy-selected hyperthermal atomic and molecular oxygen components of the incident beam (solid lines) and the hyperthermal argon beam (dashed line). The O and Ar curves have been normalized to 1.0, and the areas of the O$_2$ curve reflect the relative mole fraction of O$_2$ in the beam compared to O.](image)

Grade 22 SPI-Glas vitreous carbon samples were obtained from SPI, Inc.$^{59}$ The samples were used as is from the manufacturer, with no additional postprocessing. The samples had dimensions of 25 mm $\times$ 7 mm $\times$ 1 mm. Before introduction into the vacuum chamber, each vitreous carbon sample was cleaned with a mixture of trichloroethylene and ethanol (0.75:0.25 by volume). The vitreous carbon samples were heated using the sample mount illustrated in Figure 1b. The basic components of the mount are two water-cooled copper blocks that are electrically isolated by alumina spacers. The vitreous carbon surface was clamped to the front of the copper blocks, thus completing an electrical circuit. Current was delivered through copper water-cooling tubes and passed through the sample, heating it resistively. The desired surface temperature was achieved by adjusting the current, which ranged from 10 to 45 A, resulting in sample temperatures from 600 to 2100 K. The surface temperature was not measured directly; instead, the surface temperature was determined by fitting the TOF data from thermally scattered products to a Maxwell–Boltzmann (MB) distribution of translational energies, with temperature as an adjustable parameter. One sample was used for most of the data presented here, and this sample was subjected to one temperature cycle from 600 to 2100 K and then back to 600 K for 24 h before data collection began. The sample surface was assumed to be free of contamination based on earlier results in our lab on Ar-atom interactions with HOPG surfaces, which exhibited scattering dynamics that were indicative of a clean surface even at the relatively low temperature of 503 K.$^{50}$

**A. Temperature Dependence of Surface Reactivity.** The effect of surface temperature on the reactivity of the surface was investigated over a broad range of temperatures for fixed incidence and final angles ($\theta_i = 45^\circ$ and $\theta_f = 45^\circ$; $\theta_i = 60^\circ$ and $\theta_f = 0^\circ$). Individual TOF distributions were collected at mass-to-charge ratios ($m/z$) of 16 (O$^+$), 32 (O$_2^+$), 28 (CO$^+$), and 44 (CO$_2^+$) for 250, 250, 500, and 500 beam pulses, respectively, for each temperature. This temperature survey began with the surface at 600 K, and the temperature was increased in steps of about 100 K with a hold time of roughly 16 min at each temperature during which time TOF distributions were collected at the various $m/z$ ratios. After the temperature had reached 2100 K, the sample temperature was decreased at the same rate, with TOF distributions again being collected at each temperature step. Data were collected for two full temperature cycles from 600 to 2100 K. Each temperature cycle took about 12 h to complete.

In order to elucidate the time required to reach a steady state of oxidation at a high surface temperature (1875 K, one of the focus temperatures of our studies), the sample was held at 800 K and exposed to the hyperthermal beam for 30 min to ensure that the surface had reached a steady state of oxidation. Then the surface temperature was increased suddenly, in a matter of <30 s, to 1875 K. TOF distributions were collected sequentially for $m/z = 28, 16$, and 32 repeatedly until it was observed that the TOF distributions for $m/z = 28$ (CO$^+$) no longer changed with time, which took about 200 min.

**B. Investigation of Surface Thermal Roughening.** To investigate the effects of thermal roughening of the surface on the scattering dynamics, a beam of hyperthermal argon was directed at the surface. Ar is a useful experimental probe for studying surface roughness at the atomic level because of its relatively weak attractive potential with the surface, which makes it possible to isolate the collision dynamics to hard-sphere-like interactions. The hyperthermal Ar beam was generated using the laser-detonation source, and the synchronized chopper wheel was used to select a beam with a translational energy of 747 kJ mol$^{-1}$ and an energy width of 60 kJ mol$^{-1}$ (Figure 2). A pristine vitreous carbon sample was used for the experiments with hyperthermal Ar.

The effect of surface temperature on the scattering dynamics of hyperthermal Ar was first investigated with a procedure similar to that described in Section A. The incidence angle of the beam and the final angle of the scattered Ar were both fixed at 45$^\circ$, while the temperature was varied from 600 to 2100 K. Data were collected for 250 beam pulses per temperature.

Angular distributions of Ar, over the full range of accessible final angles, were also collected with $\theta_i = 45^\circ$ for surface temperatures of 800 and 1875 K. Individual TOF distributions were accumulated for 250 pulses. Long-term drift in the
The experiment was compensated for by sequentially varying the final detection angle from lowest to highest and then highest to lowest until two TOF distributions were collected at each final angle for a whole set of final angles. This procedure was done twice (two angular cycles) for a total of four TOF distributions for each final angle. The TOF distributions corresponding to each final angle were summed before being analyzed.

C. O/O₂ Beam–Surface Interactions. Scattering dynamics for both inelastically and reactively scattered species were measured with \( \theta_i = 45^\circ \) and \( 60^\circ \) over the full range of accessible angles at surface temperatures of 800 and 1875 K, during bombardment by the hyperthermal O/O₂ beam. TOF distributions for \( m/z = 16 \) (O⁺), 32 (O₂⁺), 28 (CO⁺), and 44 (CO₂⁺) were collected for totals of 1500, 1500, 3000, and 3000 beam pulses, respectively, for each final angle when the surface temperature was 800 K. When the surface temperature was held at 1875 K, TOF distributions were collected for totals of 1000, 1000, and 2000 beam pulses for \( m/z = 16 \) (O⁺), 32 (O₂⁺), and 28 (CO⁺), respectively. Long-term drift was compensated for in the same way described in Section B, with three angular cycles for 800 K and two angular cycles for 1875 K. The data sets at the two temperatures were normalized to take into account the different accumulation times. The \( m/z = 16 \) (O⁺) TOF distributions were corrected for dissociative ionization of O₂ during data processing by subtracting the O₂ component that fragments to \( m/z = 16 \) in the electron-impact ionizer (11% of the number density measured for \( m/z = 32 \) (O₂⁺)). The resulting TOF distributions corresponding to \( m/z = 16 \) thus represent O atoms only.

III. RESULTS AND ANALYSIS

Four species were observed leaving the vitreous carbon surface: O, O₂, CO, and CO₂. The relative abundance of each product depended strongly on the surface temperature. The scattering of volatile species was considered in terms of two limiting cases: (1) impulsive or nonthermal scattering (IS for nonreactively scattered O and O₂) and (2) thermal desorption (TD). Thermal desorption is assumed to correspond to desorbing species that can be described with a MB distribution of translational energies characterized by the surface temperature. This MB distribution is typically distinguished in the TOF distributions as a broad component at relatively long flight times. A MB distribution of translational energies, \( P(E_T) \), is converted to a number density distribution as a function of flight time, \( N(t) \), and the result is compared with the TD component of the TOF distribution. The temperature of the calculated \( N(t) \) distribution is adjusted to match the shape of the TD component. The IS/nonthermal component of a TOF distribution arises from products that scatter from the surface with translational energies that are significantly higher than the average energy in a MB distribution at the surface temperature. Products with high translational energies may come from inelastic or reactive events on the surface that occur on a time scale too short for thermal equilibrium to be attained. They

Figure 3. Time-of-flight (TOF) distributions, collected with surface temperatures from 600 to 2100 K, for the four scattered products observed following bombardment of the vitreous carbon surface with the O/O₂ beam described in Figure 2, at an angle of incidence, \( \theta_i \), of 45° and a final angle, \( \theta_f \), of 45°.
may also come from species that are initially in thermal equilibrium with the surface but desorb over a barrier. The IS/nonthermal component typically appears in a TOF distribution as a narrow peak at relatively short flight times. The TOF distribution of the IS/nonthermal component is obtained by taking the difference between the overall TOF distribution and the calculated, best-fit MB distribution.

A. Reactivity as a Function of Surface Temperature.

The scattered products were monitored as the temperature of the surface was varied. Figure 3 shows TOF distributions for O, O$_2$, CO, and CO$_2$ that were collected for different surface temperatures. The TOF distributions in Figure 3 were collected during a single pass from low to high temperature (one-half cycle, based on the description in Section A). Time zero in the TOF distributions corresponds to the time at which O atoms with the average incidence energy of 481 kJ mol$^{-1}$ collided with the surface. The most probable interaction of O atoms with the vitreous carbon surface was a nonreactive collision (Figure 3a). At lower temperatures, the TOF distributions of scattered O atoms are dominated by IS. Above 1200 K, the TD signal begins to dominate and continues to increase with increasing temperature, whereas the IS component appears to be nearly invariant with surface temperature. The TD O atoms thus account for an increase in the overall O atom flux with the vitreous carbon surface was a nonreactive collision (Figure 3a).

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Conversely, the TOF distributions for O$_2$ showed almost no change with surface temperature (Figure 3b), with IS being overwhelmingly dominant. The main reactive product was CO, and the magnitude of the TOF distributions for CO depended strongly on surface temperature. In contrast to the O and O$_2$ TOF distributions, the CO TOF distributions do not exhibit distinct nonthermal and TD components. The initial increase in temperature resulted in an increase in the CO signal; however, the signal reached a maximum at 1400 K and decreased when the surface temperature increased further. An increase in temperature did not enhance the signal from scattered CO$_2$. When the surface temperature was 600 K, the fluxes of CO and CO$_2$ were comparable: $I(t_{CO})/I(t_{CO2}) = 1.6$. Above this temperature, the CO$_2$ signal dropped dramatically and was below detectable limits at temperatures above 1100 K.

Figure 4 displays the integrated flux of the scattered products as a function of temperature. Each data point represents the average of two measurements, as the data were collected for two passes from low to high temperature and for two passes from high to low temperature. The scattered product fluxes were collected during a single pass from low to high temperature (one-half cycle, based on the description in Section A). Time zero in the TOF distributions corresponds to the time at which O atoms with the average incidence energy of 481 kJ mol$^{-1}$ collided with the surface. The most probable interaction of O atoms with the vitreous carbon surface was a nonreactive collision (Figure 3a).

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when the surface temperature is increased the temperature of maximum flux may vary from $\sim 1300$ to $\sim 1900$ K depending on the rate at which the temperature is changed. The angle-dependent TOF distributions during O/O$_2$ bombardment, described below in Section C, were collected long after a steady state had been reached, and one of the focus temperatures was 1875 K, which is very close to the temperature of maximum CO flux under steady-state conditions.

**B. Inelastic Scattering of Ar.** In order to determine if the TD O atoms described above were the result of a physical change in the surface brought about by its elevated temperature, a beam of hyperthermal Ar atoms was directed at the surface. Figure 6 displays representative TOF distributions for Ar scattering from surfaces at three temperatures, with $\theta_f = \theta_i = 45^\circ$. The surface temperature had little effect on the scattering of hyperthermal Ar. TOF distributions for every final angle and every surface temperature sampled from 600 to 2100 K only contained an IS feature. The absence of a peak at slow times ($\sim 400$ $\mu$s) in the TOF distributions indicated that Ar atoms did not scatter thermally from the surface. As seen in Figure 7, the peak flight times decreased with increasing final angle, which is indicative of structural scattering.$^{34}$ The flux-integrated angular distributions for Ar scattering from surfaces at both 800 and 1875 K surfaces were nearly identical (Figure 7b,d) and had maxima well beyond the specular angle. It is not surprising that the IS dynamics are mostly independent of surface temperature, as the interaction time between the impinging atom and the surface is so short that thermal motions hardly affect the outcome of the collision. The main effect of the increasing temperature is expected to be from the physical roughening (thermal roughening) of the surface, which would enhance multiple-bounce scattering and perhaps drive incident atoms toward thermal equilibrium. While increased thermal roughening apparently does not result in full thermalization of hyperthermal Ar atoms, both angular distributions are somewhat broad, with a full width at half-maximum of about $45^\circ$, indicating that the surface is rough in comparison to HOPG, which was shown to have a sharply peaked angular distribution beyond the specular direction.$^{30}$ In addition, the TOF distributions in Figure 6 show a slight broadening with increasing temperature, indicative of a larger range of energy transfers at the surface, albeit for IS and not TD processes. Although effects of thermal roughening can be observed in the scattering dynamics of hyperthermal Ar, there is no evidence that physical changes in the surface associated with temperature lead to significant energy loss and enhanced thermal desorption. Thus, such physical changes cannot explain the large TD signals observed in the O-atom TOF distributions in Figure 3 at higher surface temperatures.

**C. Inelastic and Reactive Scattering Dynamics during O/O$_2$ Bombardment.** Figure 8 displays representative TOF distributions, corresponding translational energy distributions, and flux-integrated angular distributions for O atoms that exited vitreous carbon surfaces held at 800 and 1875 K after colliding with $\theta_i = 45^\circ$. The flux of IS O atoms increases with final angle and reaches a maximum near $50^\circ$ before decreasing again. While the dynamical behavior and signal magnitude of the IS O atoms hardly change with surface temperature, the signal magnitude of the thermally desorbed O atoms increases dramatically at the higher temperature, as discussed above. The angular distributions of the TD O atoms appear to have maxima at the surface
normal and are fit well by a \(\cos^n\theta_i\) distribution, with \(n = 1.55\) and 1.46 for surface temperatures of 800 and 1875 K, respectively. The TOF signal at long flight times does not return to zero because of the effusive background from the source chamber. A high density of O atoms (\(\sim 10^{-3}\) Torr) is produced in the source chamber with each beam pulse, and some of these O atoms can slowly effuse through the skimmer and thermally scatter from the surface into the detector before they are pumped away by the source diffusion pump.\(^4\) The distorted slow tail in the TOF distribution makes it difficult to determine the temperature of the surface by fitting a MB distribution to the thermal desorption component in the O-atom TOF distributions. The “apparent” surface temperature is accurate to \(\pm 100\) K, meaning that the TOF distributions for the TD components could be fit well by MB distributions with temperatures from 700 to 900 K or from 1775 to 1975 K. These O-atom TOF distributions were used to determine the nominal temperatures of 800 and 1875 K, respectively. Translational energy distributions for the IS and TD components were derived from the separated TOF distributions under the assumption that the hyperthermal O-atom beam was monoenergetic.\(^4\)\(^4\) It has been shown that the translational energy distributions resulting from this procedure are broader than they should be. Furthermore, the monoenergetic beam approximation breaks down for direct inelastic scattering at angles far from surface normal when little kinetic energy is lost by the inelastically scattered atoms or molecules. This breakdown can be seen in the final translational energy distributions for nonreactive species where there are nonzero probabilities for final translational energies greater than the average translational energy of the beam. Nevertheless, the errors caused by the monoenergetic beam approximation are not significant for this experiment, and the average final energies of the scattered species are accurate.\(^4\)\(^4\) Similar to the scattered Ar atoms (Figure 7), the IS O atoms become faster at larger final angles, again indicative of structural scattering.\(^5\) The translational energy distributions for the IS O atoms are quite broad, again suggesting that that the sample surface is rough on an atomic level. The angular distributions for IS O atoms (Figure 8c,f) are broader than those observed for the scattering of Ar atoms (Figure 7b,d), which indicate scattering from a rougher surface, and might be the result of a relatively high surface coverage of O atoms.\(^3\) Another possible contribution to the broad angular distribution of IS O atoms in comparison with that of Ar might be the stronger atom–surface interaction potential of O. However, the effect of the interaction potential is apparently small compared to the effect of the surface roughness, as evidenced by the similarity between the angular distributions for IS O atoms and those for the much weaker-interacting IS O\(_2\) molecules (presented below). The angular distribution for IS O atoms is narrower at a surface temperature of 1875 K than of 800 K, suggesting that the surface became smoother at the higher temperature. Thus, it is plausible that the oxygen surface coverage decreases at higher temperatures. A decreasing oxygen coverage (i.e., less sticking) at higher surface temperatures would be consistent with the

Figure 7. Representative TOF (a,c) and flux-integrated angular distributions (b,d) for Ar atoms scattering from a vitreous carbon surface at 800 K (left) and 1875 K (right), following bombardment with the Ar beam, whose energy distribution is shown in Figure 2, at \(\theta_i = 45^\circ\). The corresponding final angles are indicated beside each TOF distribution.
increasing TD signals for O at the higher surface temperature (compare Figure 8d with Figure 8a).

In contrast to the scattering of O atoms, IS of O\textsubscript{2} was dominant at low and high surface temperatures, with TD becoming less important at the higher temperature (Figure 9). Using the estimate of 800 K for the lower-temperature surface, a MB distribution fits the slow tail of the TD component well (Figure 9a). Subtracting the MB fit at 800 K from the overall TOF distribution leads to an apparently bimodal IS component, and this bimodality is especially prominent in the corresponding translational energy distribution (Figure 9b). It is not likely that the slower "bump" in the IS component is the result of an error in the temperature used in the MB fit to the TD component. An unrealistic MB temperature of 1050 K is required to eliminate the slow bump when the MB component is subtracted from the overall TOF distribution, but when this temperature is used, the fit to the slow tail of the TD component is poor. Thus, we chose to use the temperature of 800 K for the lower-temperature MB fit because it is consistent with the fit to the slow tail of the O\textsubscript{2} TOF distributions, the results for O-atom desorption, and the observation of a dull-red glow from the sample surface that was only visible when the lights in the laboratory were turned off. The presence of two parts in the IS component suggests two dynamical pathways. The faster (or higher-energy) part of the bimodal IS component exhibits dynamics that are very similar to the IS component of the O\textsubscript{2} signal from the higher temperature surface (Figures 9d,e). The behavior of this component is analogous to that of IS O atoms (Figure 8), and we conclude that it arises from impulsive scattering of O\textsubscript{2}, which is a significant component of the incident beam (7 mol %). The slower part of the IS component appears in the data for the lower-temperature surface but is essentially absent in the data for the higher-temperature surface. We assign this extra feature to O\textsubscript{2} produced through a direct Eley−Rideal reaction between incident O atoms and O atoms residing on the surface. The disappearance of such Eley−Rideal reaction products at the higher temperature is consistent with evidence of reduced oxygen coverage at increasing surface temperatures, which implies fewer reagent O atoms at the surface. While the angular distribution of the IS O\textsubscript{2} molecules from the higher-temperature surface (Figure 9f) resembles that for O-atom scattering from lower- and higher-temperature surfaces (Figure 8c,f), with a broad maximum near $\theta_f = 55^\circ$, the angular distribution for the apparent IS O\textsubscript{2} molecules that scatter from the lower-temperature surface (Figure 9c) is nearly constant from the minimum final angle of 15$^\circ$ to about 55$^\circ$, where it then decreases rapidly with increasing final angle. Assuming

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**Figure 8.** Representative TOF (a,d), translational energy (b,e), and flux-integrated angular distributions (c,f) for O atoms from a vitreous carbon surface at 800 K (left) and 1875 K (right), following bombardment with the O/O\textsubscript{2} beam at $\theta_i = 45^\circ$. The corresponding final angles are indicated beside each translational energy distribution. Total values [for number density (a,d), energy (b,e), or flux (c,f)], nonthermal scattering (IS), and thermal desorption (TD) are represented by yellow, blue, and red colors, respectively. The TD components in (c) and (f) have been fit to $\cos^n\theta$ distributions, with $n$ given in the respective panels. The translational energy distributions of the IS and TD components (b,e) have been plotted such that their areas (or relative fluxes) may be compared for scattering at a given surface temperature. Only the shapes, and not relative fluxes, of the translational energy distributions may be compared between plots of data collected at different temperatures.
that the dynamics of IS O$_2$ are mostly independent of surface temperature, as would be expected for this nonthermal scattering process and which was confirmed by Ar- and O-atom scattering data in Figures 7 and 8, the angular distribution for the slower IS bump in the lower-temperature O$_2$ data could be approximated by subtracting the overall nonthermal O$_2$ angular distribution from the IS angular distribution obtained from the higher-temperature surface. The result suggests that the Eley–Rideal O$_2$ products scatter closer to the surface normal than the IS O$_2$, with a maximum flux at roughly $\theta_f = 20^\circ$. The translational energies of the Eley–Rideal products are tens of kJ mol$^{-1}$ (i.e., hyperthermal), but these energies are much lower than those for the IS O$_2$, which tend to be around 200 kJ mol$^{-1}$ or higher, depending on the final angle. Scattering closer to the surface normal with significant internal excitation is typical for Eley–Rideal reaction products.$^{34,41,55,56}$

The average fractional energy transfers of O and O$_2$ as a function of deflection angle, $\chi = 180 - (\theta_i + \theta_f)$, are indicative of sphere-like scattering on an atomically rough surface. Figure 10 shows the dependence of the average fractional energy transfer of IS O atoms and O$_2$ molecules as a function of $\chi$, at two surface temperatures for O and at the higher temperature for O$_2$. (Data for O$_2$ scattering from the lower-temperature surface were not used because of the difficulty in distinguishing the IS O$_2$ from the O$_2$ reaction products of an Eley–Rideal reaction.) The data for O-atom scattering in Figure 10a,b were described well by a soft-sphere model, which allows for excitation of internal modes, whose energy is designated $E_{\text{int}}/E_i$ of a collection of recoiling surface atoms with an effective mass, $m_s$.$^{38}$ The model uses two parameters, $m_s$ and $E_{\text{int}}/E_i$, where $E_{\text{int}}/E_i$ is the fraction of the incidence translational energy that goes into internal excitation of the localized collection of surface atoms and, in the case of molecular scattering, the internal excitation of the scattered molecule. In the limit of no such internal excitation, then a hard-sphere scattering model would apply. In fact, a hard-sphere model describes well the average fractional transfer of the impulsively scattered O$_2$ as a function of $\chi$ (Figure 10c). Although the higher mass and energy of incident O$_2$ might be expected to promote more internal excitation than O with the localized group of colliding surface atoms, the strong interaction potential of O compared with O$_2$ may contribute to the larger $E_{\text{int}}/E_i$ for impulsive scattering of O.
The dominant reactive product was CO (see Figure 11). The shape of the TOF distributions for CO scattering from low- and high-temperature surfaces was independent of \( \theta_i \) and consisted of a broad, structureless peak at relatively long flight times, signifying scattering dynamics that are drastically different from those of nonreactively scattered O and O\(_2\). The TOF distributions for CO were separated into nonthermal and thermal components in a manner analogous to the separation of the IS and TD components in the TOF distributions for O and O\(_2\), using the estimated temperatures of 800 and 1875 K for the two surface temperatures. Given these temperatures, the TOF distributions appeared to reflect mostly thermal scattering, but there was an additional unresolved signal at short flight times that could not be accounted for by thermal scattering at these temperatures. While this signal constitutes a nonthermal scattering component in our analysis, it is possible that a larger fraction of the CO products observed could be the result of thermal desorption if the surface temperature used for the MB distribution were in error. The CO TOF distributions from the higher-temperature surface can be fit well by a MB distribution with a temperature of 2120 K, although the distributions from the lower-temperature surface cannot be fit by a single MB distribution at any temperature. The very high MB temperature needed to fit the higher-temperature distributions and the impossibility of fitting the lower-temperature distributions suggest that at least some fraction of the CO molecules does not exit the surface in a simple thermal desorption process. The angular distributions for the total CO flux and for its assumed nonthermal and thermal components seem to have maxima toward the surface normal (Figure 11b,d). The angular distributions are very similar in shape for CO exiting the lower- and higher-temperature surfaces, but the CO flux is roughly double from the higher-temperature surface. Although the TOF distributions for CO suggest that the CO product is largely thermal, the angular distributions are much narrower than the expected \( \cos \theta_i \) distribution for thermal desorption, again suggesting a complex and possibly nonthermal process that leads to CO.

While the TOF distributions of CO scattering from the lower- and higher-temperature surfaces are similar, there is a key difference in the tails of the distributions at long flight times. The TOF distribution for CO from the higher-temperature surface goes to zero at long times, and the shape of this long tail can be fit well by a MB distribution. On the other hand, the TOF distribution for CO from the lower-temperature surface does not return to zero at long times, indicating the presence of CO molecules that do not promptly desorb within a few microseconds after the incident O atoms collide with the surface (there is no effusive background from CO in the pulsed beam source that could contribute to a slow background signal). The long tail in the TOF distribution corresponding to the lower-temperature surface can be fit well if it is assumed to be the sum of a MB component at 800 K and a convolution of a MB component with an exponential falloff having a lifetime of \( \sim 1500 \mu s \) (Figure 12). The success of this simple two-component fit suggests, but does not prove, that a fraction of the CO products on the lower-temperature surface are produced through a process that exhibits first-order kinetics.

A secondary reaction product was CO\(_2\), which was below detectable levels when the surface temperature was above 1100 K (Figure 3). Representative TOF and angular distributions for CO\(_2\) scattering from the lower-temperature surface are shown in Figure 13. Similar to the CO data, the TOF distributions for CO\(_2\) are characterized by a single, broad peak at long flight times, which could not be fit by a single MB distribution, again indicating that CO\(_2\) might be produced through thermal and nonthermal reaction mechanisms. Unlike the scattering of CO, the TOF distributions returned to zero at long times, suggesting that the reaction occurred promptly after the incident beam pulse struck the surface. The angular distributions for both components have maxima toward the surface normal and deviate significantly from a \( \cos \theta_i \) distribution.

IV. DISCUSSION

The temperature dependence of the reactive CO and CO\(_2\) signals (Figure 3) exhibits non-Arrhenius behavior, where the rate of increase in the reactivity of hyperthermal O atoms with a vitreous carbon surface apparently slows and even becomes negative with increasing temperature. As the surface temperature increases from \( \sim 600 \) to \( \sim 2100 \) K, the CO\(_2\) signal drops quickly to zero above 1100 K, and the CO signal rises to a maximum at \( \sim 1400 \) K and then decreases. In addition, the CO flux shows a pronounced hysteresis where increasing surface temperatures lead to much higher CO flux than do decreasing temperatures.
temperatures (Figure 4c). The temperature dependence of the CO signal is similar to what was observed by Olander et al. in their studies of molecular oxygen reacting with HOPG at high temperatures.\(^3\) They suggested that there are more reactive sites on the HOPG surface at lower temperatures and that these sites are removed by annealing at higher temperatures. At first the reactivity increases with temperature, but when the temperature is elevated sufficiently the number of reactive sites decreases, which hinders the reaction rate. When the temperature is decreased from a high temperature, the number of reactive sites starts relatively low and does not recover until a much lower temperature has been reached. The earlier data did not probe the nature of the reactive sites. Following the general explanation of the hysteresis by Olander et al., we would conclude that adsorbed oxygen is closely linked with the reactive sites on a vitreous carbon surface that is bombarded by O atoms. We observed that the flux of TD O atoms increases significantly with surface temperature (Figures 3 and 8), indicating less sticking of O atoms on the surface. Hence, if surface-adsorbed O atoms are required for eventual CO production, then the CO product flux would be expected to be limited by the reduced sticking of O atoms on the surface. Indeed, we do observe that the CO product flux reaches a maximum at high temperatures where the sticking of O atoms to the surface is apparently low.

The observation of significant quantities of TD O atoms is a counterintuitive result, as O atoms would be expected to be very reactive with carbon, especially if they had time to come into thermal equilibrium with the surface. One possible explanation for the TD O atoms is that incident O atoms with hyperthermal energies penetrate into the surface before desorbing. Although data on the penetration of energetic atoms or ions into vitreous carbon do not exist, data obtained for HOPG may serve as an analogue for understanding high-energy collisions with vitreous carbon. The threshold energies for Ne\(^+\) and Ar\(^+\) ions penetrating into HOPG are reported to be 32.5 ± 2.5 eV and 43.5 ± 1.5 eV, respectively.\(^5\)\(^7\) Given the masses of these two noble-gas ions, they are expected to have similar penetration thresholds as O and O\(_2\). These threshold energies are significantly higher than the maximum translational energies of the O and O\(_2\) in the incident beam, which are 5.7 eV (O) and 11.5 eV (O\(_2\)). Furthermore, it is unlikely that extreme temperatures would significantly change the values of these threshold energies. This supposition is reinforced by the fact that Ar atoms scatter only impulsively and that the Ar scattering dynamics remain essentially unchanged with surface temperature (Figure 7). It has been shown that atoms penetrating into a surface have substantially different scattering dynamics than atoms that simply scatter impulsively from the surface.\(^5\)\(^8\) Thus, we conclude that the thermal O atoms exiting the surface do not originate from O atoms that have penetrated the surface.

Instead of penetration, one might imagine that incident O atoms could become momentarily trapped in pores at the surface and lose most of their energy before desorbing.

Figure 11. Representative TOF (a,c) and flux-integrated angular distributions (b,d) for CO molecules scattering from a vitreous carbon surface at 800 K (left) and 1875 K (right), following bombardment with the O/O\(_2\) beam at \(\theta_i = 45^\circ\). The corresponding final angles are indicated beside each TOF distribution. Total values [for number density (a,c) or flux (b,d)], nonthermal scattering, and thermal desorption are represented by yellow, blue, and red colors, respectively.
Although vitreous carbon comprises closed pores and is considered impenetrable to gases,\textsuperscript{6,7} the porous structure of vitreous carbon may be exposed by removal of carbon in the form of CO and CO\textsubscript{2}. Even if O atoms become adsorbed to all exposed reactive sites, the residual rough, porous structure could conceivably lead to multiple collisions and enhanced trapping of O atoms at the surface. An increased surface temperature might be expected to increase the reactivity and lead to a more porous structure at the surface and therefore to more trapping of O atoms. However, the temperature dependence of the TD O-atom signal is reversible, so if a porous structure were revealed at high temperatures it should still persist at low temperatures and lead to the same mechanical trapping of O atoms. The fact that the TOF signals at low and high surface temperatures are reproducible through several cycles of heating and cooling is therefore at odds with the idea that the opening of pores in the vitreous carbon could be the explanation for the thermal O-atom signal that grows with increasing surface temperature.

Thermal roughening of the surface would be a potential way to drive incident O atoms into thermal equilibrium with the surface that could explain both the increase in TD O atoms at higher temperatures and the reversibility in the TOF signals with temperature. It has been observed that modest increases in the temperature of a liquid surface bombarded by noble-gas atoms can lead to a higher fraction of thermally desorbing atoms.\textsuperscript{59} However, the dependence of the Ar scattering dynamics on temperature discounts this possibility. The hyperthermal beam of Ar atoms (747 kJ mol\textsuperscript{-1}) was more energetic than the hyperthermal beam of O atoms (481 kJ mol\textsuperscript{-1}), so the colliding Ar atoms would need to lose more energy than the O atoms in order to come into thermal equilibrium with the surface; thus, a lower fraction of Ar atoms would be expected to scatter from the surface with thermal energies. Nevertheless, if thermal roughening were the explanation for the strong thermal O-atom signal at high temperatures, then the Ar TOF distributions should show at least a small TD component that increases with surface temperature, which they do not. The only apparent effect of thermal roughening on the Ar scattering data is in the width of the Ar TOF distributions, which does increase slightly with surface temperature. The temperature-dependent increase in the width of translational energy distributions for impulsive scattering has been observed previously.\textsuperscript{60} The subtle increase in the width of the Ar TOF distributions with increasing surface temperature (Figure 6) is a thermal roughening effect of mechanical surface roughening, then we conclude that it must be the result of the unique chemical interactions between incident O atoms and the vitreous carbon surface. The strength of those interactions relative to the Ar–surface interaction potential is no doubt the reason for the dramatically different scattering dynamics observed for the two atoms.

As suggested at the beginning of this section, the substantial increase in the TD flux of O atoms with temperature implies decreasing oxygen coverage as the surface temperature is
increased (during steady-state O-atom bombardment). Thermal and nonthermal interaction pathways were apparent at all temperatures; however, the dominant scattering mechanism of the O atoms changed, for example, from IS at 800 K to TD at 1875 K, and the overall flux of O atoms increased significantly. The comparison of O and O$_2$ scattering dynamics also supports the conclusion of a reduced coverage at the higher temperature.

The angular distributions for the IS O atoms were similar at 800 and 1875 K; both were peaked past the surface normal and had similar intensities and widths. The near invariance in the IS O angular distributions with temperature is in contrast to the nonthermal scattering of O$_2$, where the angular distribution from the 800 K surface is much broader than that from the 1875 K surface. The broader angular distribution at the lower temperature was attributed to an Eley–Rideal reaction, which provides an additional pathway to produce scattered O$_2$. The apparent absence of this reaction at the higher surface temperature is consistent with the conclusion that the increased flux of TD O atoms reflects a lower surface coverage of oxygen, as a reduced coverage would result in fewer O atoms on the surface that are available to react with incident O atoms.

Computational studies have shown that an Eley–Rideal reaction to produce O$_2$ is the primary reaction pathway on an HOPG surface during oxidation by O atoms. In an earlier study in our laboratory on hyperthermal O-atom interactions with a 503 K HOPG surface, we attributed much of the O$_2$ signal to an Eley–Rideal reaction, thus demonstrating consistency between the experimental and theoretical results. Recently, Morón et al. have challenged this assignment, and we now agree that the earlier attribution of a significant fraction of the O$_2$ signal to an Eley–Rideal reaction was incorrect because a detailed consideration of the data for the observed nonthermal O and O$_2$ reveals that the scattering dynamics for these two products were similar and are best interpreted as impulsive scattering from a smooth surface. Thus, we no longer believe that our earlier data support the computational results that the Eley–Rideal reaction to produce O$_2$ is the dominant reaction pathway under continuous bombardment of an HOPG surface by hyperthermal O atoms. Furthermore, our new results clearly indicate that this reaction is only a minor reaction pathway when hyperthermal O atoms bombard a vitreous carbon surface under steady-state conditions at 800 K and that this reaction is essentially absent at 1875 K. The dominant components of the O$_2$ TOF distributions at both high and low temperature have nearly the same TOF distribution as the IS O atoms. In the abstraction of an O atom adsorbed on the surface by an impinging O atom, it has been shown that a large fraction of the available energy is partitioned into internal modes (i.e., vibrational and rotational excitation), which results in a lower final translational energy and a broader angular distribution than would be observed for an O$_2$ molecule that is scattered impulsively from a surface.

Accordingly, the peak at earliest times in the TOF distributions depicted in Figure 9a,d is assigned to IS O$_2$ that is not the result of a reactive process. When the surface was at 800 K, there was an additional nonthermal component at intermediate energies between the IS and TD components. This intermediate component reflects O$_2$ molecules that leave the surface with relatively low translational energies, which would be consistent with the high internal excitation that has been reported for an Eley–Rideal reaction. In addition, the broadening of the angular distribution for nonthermal O$_2$ at 800 K (Figure 9c) suggests that the intermediate O$_2$ component has a maximum away from the surface normal yet below the specular angle, which is also consistent with an Eley–Rideal reaction.

Unlike O-atom desorption, the flux of the TD O$_2$ shows a modest decrease with increasing surface temperature (Figure 9). O$_2$ is bound to the surface by a small barrier (0.1 eV), indicative of physisorption, and has a very low sticking coefficient (10$^{-14}$), so it is expected to scatter without reacting. Indeed, it appears that most of the O$_2$ scatters impulsively; however, there is still clear evidence of a relatively low flux of TD O$_2$ which must come either from a nonreactive process that leads to thermal desorption or from a reaction that produces O$_2$ that desorbs thermally. Larciprete et al. have shown that it is possible to produce thermal O$_2$ from the cyclic addition of O atoms in epoxide groups present on the surface. If the TD O$_2$ was the result of such a reaction or from thermal recombination of O atoms on the surface, then the flux of TD O$_2$ should decrease at increasing temperatures as the surface coverage of oxygen decreases, which is consistent with our data. It is thus possible that the TD O$_2$ signal that we observe is the result of recombination reactions involving O atoms on the surface. But we cannot rule out the possibility that some, or even all, of the TD O$_2$ signal that we observe is not the result of a reactive process but rather from O$_2$ that either physisorbs momentarily to the surface or loses sufficient energy to desorb thermally without physisorption.

The decrease in surface oxygen coverage with temperature is inextricably linked with the ultimate decrease in the reaction probability of O atoms on the vitreous carbon surface at high temperatures. As discussed above, the Eley–Rideal reaction of incident O atoms with surface oxygen atoms to produce O$_2$ is essentially absent at a relatively high surface temperature of 1875 K. The Eley–Rideal reaction is nonthermal and should not depend on surface temperature, but as we do see this reaction disappear with increasing temperature, we must conclude that the surface oxygen coverage decreases with temperature. The flux of the main reaction product, CO, increases with surface temperature but then begins to decrease above ~1900 K (under steady-state conditions). The flux of the CO$_2$ reaction product drops quickly with increasing surface temperature and is below detectable levels above 1100 K. The reaction processes that lead to the main reaction product, CO, appear to be mostly thermal, based on the preponderance of slower products in the TOF distributions. Therefore, if Arrhenius behavior were applicable, the reaction probability to produce CO should increase with surface temperature. In fact, the CO flux does increase with surface temperature, but it reaches a maximum at 1900 K and then begins to decrease. We surmise that the increasing reaction probability competes with the decreasing availability of surface O atoms as the temperature increases. The decrease and eventual disappearance of CO$_2$ with increasing surface temperature may be partially the result of the Boudouard reaction, CO(g) + C(s) → 2CO(g), which is discussed below. Perhaps more important is the fact that the production of CO$_2$ requires more surface O atoms than does the production of CO; thus, the CO$_2$ yield would be expected to decrease with increasing temperature as the surface O atoms are depleted. The reduction in CO$_2$ yield could be enhanced if the increasing surface temperature leads to more rapid desorption of the CO product because the formation of CO would be the required first step in the stepwise production of CO$_2$. The Boudouard reaction may explain the long tail in the CO TOF distributions collected from the 800 K surface (see...
Figures 11 and 12). This long tail indicates that not all of the CO product formation occurred promptly after the beam pulse struck the surface. It is possible that a fraction of the nascent CO2 goes on to react with the surface to form CO through the Boudouard reaction, which is highly endothermic ($\Delta H = 172$ kJ mol$^{-1}$) and becomes entropically favored at temperatures greater than 700 °C. At 800 K, a small portion (≈10%) of the CO2 products formed through reactions between incoming O atoms and the oxidized surface could be converted to CO. In addition, only the CO2 products that remained on the surface long enough to react with a carbon site would be able to react and produce CO. Consequently, the fraction of CO produced through the Boudouard reaction would be expected to be a minor fraction of the overall CO product. The long tail observed in the CO TOF distributions did indeed represent a minor fraction of the CO product (Figure 11c), and such a tail was not evident in the TOF TOF distributions at 1875 K or in the TOF distributions for CO (Figure 13). As indicated in Figure 12, the long tail in the CO TOF distribution was fit well under the assumption that slow CO was produced through a first-order (or pseudo-first-order) process with a lifetime of ≈1500 ns. The reaction rate of the Boudouard reaction at 800 K is not well-known, but there is some evidence that this reaction is slow, which would be consistent with the lifetime that we derived. The simultaneous observation of a long tail in the CO TOF distributions and absence of such a tail in the CO2 TOF distributions is also consistent with the Boudouard reaction, as this reaction could lead to a slow CO product without affecting the observed scattering dynamics of unreacted CO2 products. As the temperature of the surface increases, the fraction of CO2 that would be reduced through the Boudouard reaction would be expected to increase, giving rise to more CO with long apparent residence times on the surface. At higher surface temperatures, the thermal desorption of O atoms would limit the production of CO2 and close the Boudouard channel for the secondary formation of CO which is consistent with the absence of a long tail in the TOF distributions for CO at 1875 K. While our results suggest the intriguing possibility that the Boudouard reaction plays a role in the oxidation of carbon at elevated temperatures, further work would need to be done to confirm this tentative conclusion.

Computational studies have attempted to elucidate the reaction mechanisms for the gasification of carbon by O atoms. These studies have focused on HOPG as a model surface. It is expected that similar surface chemistry will take place on vitreous carbon because vitreous carbon has a large aromatic ring network similar to that of HOPG. The first step in the production of CO and CO2 is the adsorption of an oxygen atom to the surface. Some O atoms will react with carbon atoms on the surface to form semiquinone and lactone precursor sites. Oxygen adatoms migrate across the surface, forming transient bonds with carbon atoms during their migration, and react at a semiquinone or lactone site to produce CO or CO2. Excess O atoms surrounding the reactive sites lower the barriers and endothermicities for reactions to produce both CO and CO2, with more O atoms being required to lower the endothermicity for production of CO2 to a given value. Thus, these theoretical studies suggest that adsorbed O atoms are required for the production of CO and CO2 and that more adsorbed O atoms are required to produce CO2 than are required to produce CO. The competition between CO and CO2 may be related to adsorbed O atoms in additional ways. The transient C–O bonds that are formed as an O atom migrates across the surface are weaker than the underlying C–C bond, making their breakage more favorable. At high temperatures, a C–O bond may cleave and release the O atom back into the vacuum. A recent study suggests that this process may be aided by local O-atom collisions. The consequence of C–O bond cleavage and escape of O atoms back into the gas phase is that O atoms desorb from a high-temperature surface before arriving at the precursor sites, which hinders the formation of CO and CO2 produced through an indirect reaction mechanism. Again, because more O atoms are required for the formation of CO2 any escape of O atoms before they can reach a reactive site will preferentially suppress the formation of CO relative to that of CO. These theoretical results are consistent with our experimentally derived deductions about the temperature-dependent reaction probabilities to form CO and CO2, discussed above, and they offer some insight into the mechanism through which O atoms desorb thermally with increasing likelihood as the surface temperature is increased. Desorption barriers for CO and CO2, predicted for thermal oxidation of graphite, can lead to products with higher-then-thermal translational energies and relatively narrow angular distributions that peak near the surface normal. Thus, such activated desorption processes might be responsible for the apparent nonthermal CO and CO2.

V. CONCLUSION

The dynamics of the interactions of O and O2 with a vitreous carbon surface at high temperatures have been investigated with the use of a beam-surface scattering technique. Nonreactive O and O2 and reactive O2, CO, and CO2 products were detected following bombardment of a vitreous carbon surface with a beam containing hyperthermal O and O2. The dynamical behavior of these products was surveyed with a range of surface temperatures from 600 to 2100 K and investigated in detail at 800 and 1875 K. Nonreactive O and O2 were observed to exit the surface through impulsive scattering and thermal desorption channels. The flux of O atoms that scattered from the surface with thermal energies increased dramatically with the temperature of the surface, while the flux of impulsively scattered O atoms remained essentially constant with temperature. Whereas the thermally scattered O atoms represented a small fraction of the products scattered at the lower temperatures, they were overwhelmingly dominant at higher surface temperatures. Nonreactive O2 exited the surface mostly through impulsive scattering at all temperatures, with only a small fraction accommodating to the surface temperature before desorbing thermally. The increase in thermally scattered O atoms reflects a decrease in oxygen coverage on the surface, which ultimately limits the reactivity of incident O atoms with the surface. The major reaction product was CO, and the probability to produce CO increased with temperature to a maximum at ~1900 K (under steady-state bombardment conditions) and then decreased as the temperature was increased further. The reaction probability to produce CO2 was comparable to that of CO at 600 K, but it dropped rapidly with increasing temperature and disappeared above 1100 K. Both the CO and CO2 products were apparently formed through nonthermal and thermal mechanisms, but these products were most likely to exit the surface with translational energies characteristic of the surface temperature, implying that the underlying reaction mechanisms are mainly indirect. The direct (Eley–Rideal) reaction of incident O atoms with surface-adsorbed O atoms to
produce O₂ was found to be a minor reaction pathway, in contradiction to the results of theoretical studies on HOPG. Evidence has been found for a secondary reaction of nascent CO₂ products with the carbon surface to produce CO, although the suggested Boudouard mechanism remains equivocal. The counterintuitive result that the reactivity of the surface decreases at high temperatures is a consequence of the desorption of O atoms at high surface temperatures, which diminishes the indirect reactions that produce CO and CO₂ and suppresses the overall reactivity of the surface.

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**Notes**
The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work has been supported by the Air Force Office of Scientific Research: FA9550-10-1-0563. V.J.M. is grateful for support from the Department of Defense (DoD) through the National Defense Science & Engineering Graduate Fellowship (NDSEG) Program.

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