Direct Observation of the Crossover from Single to Multiple Excitations in Femtosecond Surface Photochemistry

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Laser pulses of 110 fs duration at 310 nm are used to desorb O_2 from a Pt(111) surface over a range of laser fluences which encompasses the single electronic excitation regime at low fluences and the multiple excitation regime at high fluences. The crossover between regimes is apparent in both the desorption yield and the translational energies of the desorbing molecules. Similar results are obtained for O_2 coadsorbed with CO, where irradiation also produces CO_2, with a O_2/CO_2 branching ratio which changes by 2 orders of magnitude between regimes. The results are compared to those contained using 8 ns, 355 nm and 90 fs, 620 nm laser pulses. [S0031-9007(96)00918-0]

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Recent experiments have shown that irradiation by subpicosecond laser pulses leads to desorption induced by multiple electronic transitions (DIMET) [1–8], which contrasts with conventional photochemistry using longer pulses and lower intensities (DIET) [9,10]. The single nonthermal excitation in the DIET regime leads to linear dependence of the yield and independence of the final-state distributions on the laser fluence (energy per unit area). In DIMET, the high degree of electronic excitation at the surface produces an enhancement of the desorption yield, a nonlinear dependence of the yield on the laser fluence, different branching ratios between competing reaction pathways, and translational energy distributions of desorbed molecules which vary with fluence.

The existing data and discussions to date have fallen into one of these two regimes of single vs multiple excitations. However, a unified picture including a crossover between the two regimes is conceptually desirable and provides a more complete understanding of an overall photochemical mechanism which is applicable for all types of radiation. With nanosecond lasers, it is difficult (if not impossible) to reach the DIMET regime without heating (thermal effect) or ablating the substrate. In this Letter, we show convincingly that the crossover from the DIMET to the DIET regime is revealed by decreasing the fluence of 110 fs laser pulses at 310 nm and measuring three characteristic properties of the desorbed molecules: yield, translational energy, and reaction branching ratio. The crossover is demonstrated for the photochemically active systems of O_2 molecularly adsorbed on Pt(111), and O_2 coadsorbed with CO on Pt(111); these systems have been shown to exhibit many important aspects of surface photochemistry [11,12].

The experiments were carried out in an ultrahigh vacuum chamber equipped with low energy electron diffraction (LEED) optics and a quadruple mass spectrometer (QMS). The clean Pt(111) at 67 K was dosed with $^{18}O_2$ to saturation coverage using a microcapillary array. The coadsorbate system was subsequently prepared with an equal dose of $^{13}C^{18}O$. Femtosecond laser pulses were produced at a repetition rate of 10 Hz by an amplified colliding-pulse mode-locked laser operating at 620 nm, with a pulse duration of 90 fs (FWHM). Pulses at 310 nm with duration 110 fs were obtained by frequency doubling in a 150 μm thick BBO crystal. The *p*-polarized light was incident on the sample at 50°, with a top-hat intensity profile. The beam quality was verified by scanning a pinhole and photodiode detector across the beam outside the vacuum chamber in a plane equivalent to the sample location. Time-of-flight (TOF) distributions of the desorbed molecules were detected along the surface normal by the QMS operating in pulse counting mode, with a $\pm 3\%$ uncertainty in the measured flight times due to the finite ionizer size. The fraction of molecules desorbed per laser pulse was kept below 10^{-2} monolayer/pulse to minimize gas-phase collisions. Photodesorption was also induced using the 355 nm, 8 ns pulses of a *Q*-switched Nd:YAG laser, at intensities held sufficiently low to limit transient surface heating to <40 K, so that desorption proceeds photochemically rather than thermally. Similarly, the fluence of femtosecond laser pulses was limited to 2.5 mJ/cm^2 to ensure no significant heating of the substrate. All the reported data are consistent with the nonthermal mechanisms.

The crossover from a single excitation process to a multiple excitation process is most readily observed in the O_2 yield as a function of laser fluence shown in Fig. 1. The photoyield (molecules detected per laser pulse) produced using 310 nm irradiation is linear in laser fluence at low fluences, and then switches to a nonlinear dependence near 0.5 mJ/cm^2. In the low fluence regime, the O_2 photoyield is in good quantitative agreement with that of conventional photodesorption. This can be seen by comparing the 310 nm photoyield curve to photoyields produced by 8 ns, 355 nm pulses, also shown in Fig. 1. The O_2 photoyield at 310 nm is larger than that at 355 nm by a factor of ~2, in accord with the previously measured wavelength dependence [12]. In the high fluence regime,

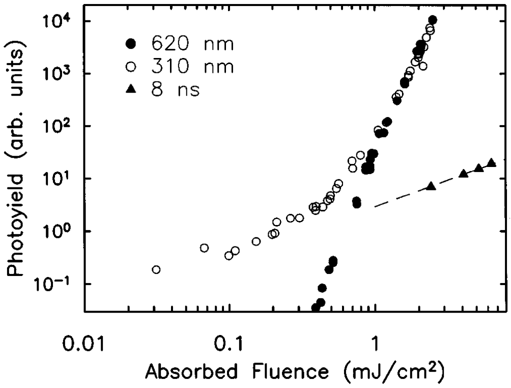

FIG. 1. Photoyield versus absorbed laser fluence for $^{18}O_2$ desorbed from $^{18}O_2/Pt(111)$ at 67 K using 110 fs, 310 nm pulses, 90 fs, 620 nm pulses, and 8 ns, 355 nm pulses.

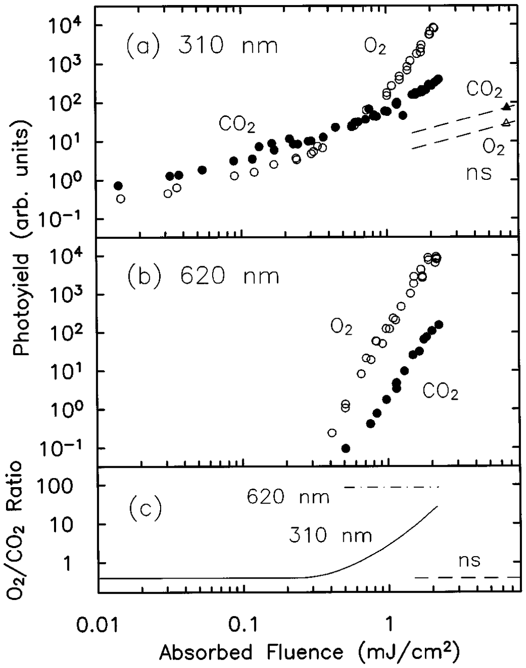

FIG. 2. Photoyield versus absorbed laser fluences for $^{18}O_2$ and $^{13}C^{18}O_2$ desorbed from $^{13}C^{18}O_2/^{18}O_2/Pt(111)$ using (a) 110 fs, 310 nm pulses and 8 ns, 355 nm pulses, and (b) 90 fs, 620 nm pulses. The 310 nm O_2/CO_2 branching ratio (c) changes from the 355 nm value toward the 620 nm value as the fluence increases.

the 310 nm photoyields are in good agreement with the photoyields produced using 620 nm irradiation, which follow a power law dependence given by $Y \propto F^{6.3\pm0.5}$. Crossover to a linear regime is also expected with 620 nm irradiation. However, extrapolation of the wavelength dependence [12] to 620 nm gives a first order cross section which is ~100 times lower than that at 310 nm. This is just below the detection limit.

The results from $CO/O_2/Pt(111)$ are qualitatively similar to those of the single adsorbate system, except the three laser sources also induce CO_2 production and desorption. The 310 nm O_2 and CO_2 desorption yields, shown in Fig. 2(a), vary linearly with absorbed fluence in the low fluence regime, and are in good agreement with the yields obtained with 355 nm, 8 ns laser pulses. At higher fluences, the O_2 and CO_2 yields crossover to a nonlinear regime where they are in good agreement with yields obtained using 620 nm, 90 fs pulse irradiation, shown in Fig. 2(b). Most notable in Fig. 2(a) is the change in the relative O_2 and CO_2 yields with 310 nm, 110 fs irradiation which occurs near the crossover fluence. At low fluences, CO_2 yield measured normal to the surface is larger than the O_2 yield with a branching ratio of $O_2/CO_2 \simeq 0.4$, as it is in the case of 355 nm, 8 ns irradiation. Near the crossover fluence, the branching ratio changes by several orders of magnitude and approaches the 620 nm value of $O_2/CO_2 \simeq 80$, as seen in Fig. 2(c). This change in the O_2/CO_2 branching ratio under subpicosecond UV irradiation was also reported in Ref. [13], although they were unable to probe fluences low enough to observe the linear limit for O_2 desorption, and thus did not associate the change in branching ratio with the crossover from single to multiple excitations.

The crossover can also be observed in the fluence dependence of the O_2 translational energy distribution. Figure 3(a) shows a TOF spectrum of O_2 desorbed from $O_2/Pt(111)$ by 310 nm, 110 fs laser pulses at a fluence of 0.7 mJ/cm^2, which is just above the crossover fluence shown in Fig. 1. At this fluence, the spectrum is well fit by a modified Maxwellian distribution [14] of the form $f(t) = t^{-4}\exp(a/t^2 + b/t + c)$ with flux-weighted mean translational energy $\langle E\rangle/2k_B = 640$ K and reduced width $w \equiv [2(\langle E^2\rangle/\langle E\rangle^2 - 1)]^{1/2} = 1.06$. The distribution shows a remarkable variation with fluence, as shown in Fig. 4. At low fluences, $\langle E\rangle/2k_B$ is constant, as is expected with a single excitation process, and the value $\langle E\rangle/2k_B \simeq 850$ K obtained using 310 nm, 110 fs pulses is only slightly higher than the value of $\langle E\rangle/2k_B \simeq 805$ K obtained using 8 ns, 355 nm laser pulses, and is due to the difference in the wavelengths. At the crossover fluence of 0.5 mJ/cm^2, the mean translational energy decreases rapidly to a new value of $\langle E\rangle/2k_B \simeq 640$ K and then begins to increase again in the high fluence region, where the 310 nm mean translational energies are in good agreement with those obtained using 620 nm, 90 fs irradiation, also shown in Fig. 4. This phenomenon of translational energies which increase with laser fluence under subpicosecond laser pulse irradiation, which is well illustrated by the 620 nm data in Fig. 4, was first reported in Ref. [7], and was attributed to the strong influence of the substrate electronic temperature at the time of desorption. The O_2 translational energies from $CO/O_2/Pt(111)$ exhibit similar variations with fluence, albeit with higher mean translational energies; for example, $\langle E\rangle 2k_B \simeq 845$ K in Fig. 3(b).

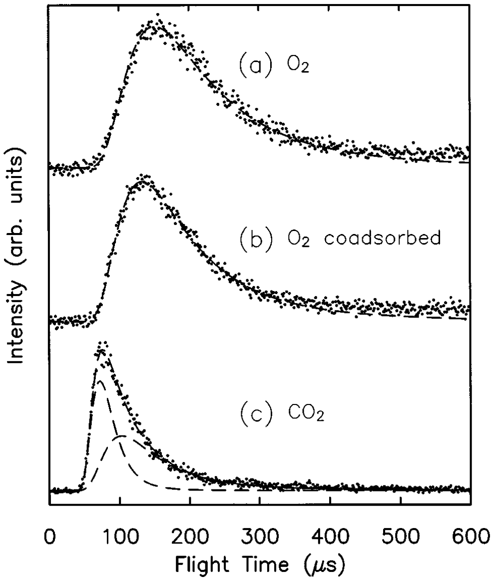

FIG. 3. TOF spectra acquired with 110 fs, 310 nm, 0.7 mJ/cm^2 laser pulses, at substrate temperature 67 K for (a) $^{18}O_2$ desorbed from $^{18}O_2$/Pt(111), and (b) $^{18}O_2$ and (c) $^{13}C^{18}O_2$ desorbed from $^{13}C^{18}O$/$^{18}O_2$/Pt(111). The dashed lines in (a) and (b) are fits by modified Maxwellian distributions with $\langle E\rangle/2k_B = 640$ K, $\omega = 1.06$ and $\langle E\rangle/2k_B = 845$ K, $\omega = 1.04$, respectively. The $^{13}C^{18}O_2$ TOF spectrum is fit by the sum of two distributions with total $\langle E\rangle/2k_B = 2950$ K.

Figure 5 shows the mean translational energy of photodesorbed CO_2 as a function laser fluence using 310 nm, 620 nm, and 355 nm pulsed irradiation. To adequately fit the TOF spectra, the sum of an ordinary Maxwellian and a modified Maxwellian was required, and the reported values of $\langle E\rangle/2k_B$ are the mean energy from both distributions; see Fig. 3(c). Under 310 nm irradiation, $\langle E\rangle/2k_B$ remains constant over the entire fluence range, and the value of $\langle E\rangle/2k_B = 2950$ K is in good agreement with the value of $\langle E\rangle/2k_B = 2830$ K obtained with 355 nm irradiation. In contrast, the CO_2 mean translational energy obtained with 620 nm, 90 fs irradiation is significantly lower, and increases slightly with fluence. The relatively constant value of the CO_2 mean translational energy under 310 nm irradiation can be understood through inspection of Fig. 2(a). The CO_2 yield remains linear over most of the fluence range shown and begins to enter the nonlinear regime only at the highest fluences used. Thus CO_2 is desorbed via a single excitation mechanism over most of this range of 310 nm fluences, and a constant translational energy distributions is expected.

Although little difference is seen in Figs. 1, 2, and 4 between the 310 and 620 nm photoyields, branching ratio, and translational energies at high fluences, we must point out that the 310 nm intensity profile at the sample was only *approximately* top hat, which leads to some ambiguity in the determination of fluence. While we attempted to factor the beam profile into the fluence calculation, the 310 nm fluences presented could be incorrect by an overall multiplicative factor as high as 30%. Thus we cannot decisively conclude that the results obtained with 310 and 620 nm irradiation are truly equal in the high fluence regime. However, when taken in combination, the agreement between the 310 and 620 nm yields, translational energies, and branching ratios in the multiple excitation regime supports the argument that the two wavelengths are equivalent. It is unlikely that the results at 310 and 620 nm could truly differ, but in such a way that they could be brought back into apparent agreement by a single multiplicative factor influence.

There is some dispute on whether the 310 and 620 nm photoyields are indeed equal in the multiple excitation regime. References [4] and [8] report power-law exponents near 6 for the fluence dependence of the O_2 yield obtained with laser pulses in the red and near-IR, in good agreement with the results presented here, but significantly lower power-law exponents obtained with UV pulses. The difference between Refs. [4] and [8] and this Letter cannot be attributed to the possible error in the UV fluence measurement, noted above, by an overall multiplicative factor, which does not affect the

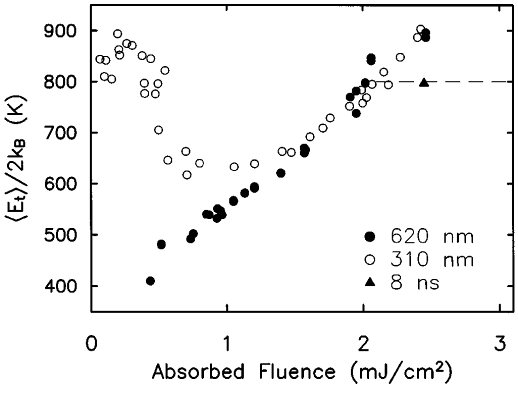

FIG. 4. Mean translational energy versus absorbed laser fluence for $^{18}O_2$ desorbed from $^{18}O_2$/Pt(111) using 110 fs, 310 nm pulses, 90 fs, 620 nm pulses, and 8 ns, 355 nm pulses.

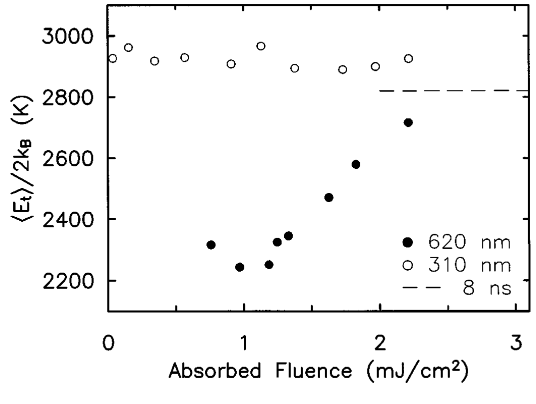

FIG. 5. Mean translational energy versus absorbed laser fluence for $^{13}C^{18}O_2$ desorbed from $^{13}C^{18}O$/$^{18}O_2$/Pt(111) using 110 fs, 310 nm laser pulses, 90 fs, 620 nm laser pulses, and 8 ns, 355 nm laser pulses.

power-law exponent. Currently, no definitive explanation can be given to explain this discrepancy; however, several differences in the experimental arrangements favor the results presented here. References [4] and [8] used non-top-hat beam profiles, which can complicate the analysis. Also, only high desorption yields, ranging from ~5% to full desorption, could be probed in Refs. [4] and [8] with UV pulses. Determination of the power-law exponent is difficult near the full-desorption limit, as the power-law dependence naturally breaks down. The highest yields in Fig. 1 correspond to ~1% desorption.

Typical approaches to modeling in the high fluence regime, such as DIMET [15,16] or frictional heating [17,18], assume a desorption process mediated by laser excited substrate electrons which can be characterized by an electronic temperature $T_e(t)$. The good agreement between the 310 and 620 nm results in the multiple excitation regime is consistent with this assumption, since in the case of Pt, $T_e(t)$ differs little at these wavelengths for a given absorbed fluence. Unlike Refs. [4] and [8], little evidence is seen for a role played by nascent electrons (laser excited electrons which have not yet "thermalized") except at fluences near or below the crossover fluence, where a clear difference between the 310 and 620 nm results is observed.

Figure 4 is remarkable in that there is a region near 0.5 $\mathrm{mJ/cm^2}$ where the O_2 mean translational energy *decreases* with increasing fluence. This rapid decrease must occur since the mean translational energy for nanosecond irradiation is about twice that for femtosecond irradiation at 620 nm and 0.5 $\mathrm{mJ/cm^2}$. At all fluences, both single and multiple excitations contribute to the photochemistry. For fluences above the crossover, the multiple excitation mechanism overwhelms the single excitation mechanism. The nonlinear effect becomes insignificant compared to the linear effect for fluences below the crossover. The threshold for conventional photodesorption involving single excitation lies near 420 nm (photon energy $\hbar\omega \simeq 3.0$ eV) [11,12]. In contrast, irradiation with 620 nm, where only multiple excitations are observed, leads to peak electronic temperatures of $k_B T_e < 0.2$ eV. This significant difference in the electron energies suggests that two distinct excited electronic states are involved in the single and multiple excitations regimes. This possibility was also proposed in the closely related system of O_2/Pd(111) for providing a rationale for different branching ratios in the two regimes [19]. Excitations of a substrate electron to the higher lying $3\sigma_u^*$ level [11,12] and the lower lying $2\pi^*$ level [7,16] of the adsorbed O_2 are proposed for the single excitation and the multiple excitations, respectively.

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