Observation of an isotope effect in femtosecond laser-induced desorption of \( \text{O}_2/\text{Pd}(111) \)

Daniel P. Quinn and Tony F. Heinz

Department of Physics, Columbia University, New York, New York 10027

(Received 16 December 2002; accepted 14 April 2003; published 1 July 2003)

Femtosecond laser pulses can induce desorption of oxygen adsorbed in the molecular state on Pd(111) surfaces. In this study, the behavior of the \( ^{16}\text{O}_2 \) and \( ^{18}\text{O}_2 \) isotopic species is characterized for the saturated Pd(111) surface at a base temperature of 95 K. The \( ^{16}\text{O}_2 \) species is found to desorb with a yield \( 1.8 \pm 0.3 \) times greater than that of the \( ^{18}\text{O}_2 \) species. The implications of this finding for the desorption mechanism are discussed. © 2003 American Vacuum Society.

[DOI: 10.1116/1.1580486]

I. INTRODUCTION

The use of different isotopes of a given adsorbed species provides a powerful probe of the dynamics of nonequilibrium surface processes. The utility of such measurements rests on the fact that the electronic potential energy surfaces are essentially unaltered by variation of the mass of adsorbed species, while the nuclear dynamics on a specified potential energy surface change in a well-defined manner. The situation is illustrated by the predictions of the semiclassical Menzel–Gomer–Redhead (MGR) model\(^1,2\) for desorption induced by electronic transitions (DIET).\(^3\) This picture provides an understanding of how a slight change in the isotopic mass can give rise to a dramatic change in desorption yields: For small desorption probabilities, the modest increase in velocity on the excited-state potential energy surface associated with a lower isotopic mass leads to an exponentially enhanced desorption yield. The analysis also provides a means of inferring from the isotope effect a key parameter in the desorption process, namely, the probability of desorption of the adsorbed species upon electronic excitation. This possibility has been exploited in several studies of electronically induced desorption over the years.\(^4–8\)

In this work, we examine the nature of the isotope effect for desorption in a regime different from that of traditional electronically induced processes. Under conventional conditions, whether driven by impinging electrons or photons, the rate of excitation is sufficiently low that only single-excitation processes are relevant. One observes a desorption rate that is linear in the flux of exciting electrons or photons. A different regime is entered through the use of surface excitation by femtosecond laser pulses.\(^9–25\) This regime displays characteristics distinct from both those of conventional surface photochemistry that prevails for low excitation densities and from those of simple transient heating of the substrate that prevails for laser pulses of longer duration. A central feature of femtosecond laser-induced surface processes on metals is the decoupling of the substrate electronic and lattice excitations. This leads to the possibility of high transient electronic temperatures with relatively little lattice heating.\(^14,17,23\) Analyses of the yield and energy distribution of species desorbed under such excitation indicate that adsorbate coupling to the highly excited substrate electrons is frequently responsible for the observed desorption or reaction processes. Two-pulse correlation measurements in the time domain provide direct support for this conclusion by demonstrating the short lifetime of the excitation responsible for the surface process.\(^10,14,17\)

In the regime of femtosecond excitation, there have been few studies to date of the isotope effect. Mazur and collaborators\(^20\) examined isotope effects for the \( \text{O}_2/\text{Pt} \) system, with the principal aim of distinguishing between dissociative/associative and molecular desorption channels by isotopic labeling. In a recent investigation of a surface reaction by Bonn \textit{et al.},\(^22\) isotopic substitution was used to elucidate the relative importance of electronic and phononic excitation of adsorbates participating in a bimolecular reaction. On the other hand, in measurements of \( \text{NH}_3(\text{ND}_3)/\text{Pt}(111) \) under femtosecond excitation, no isotope effect was observed.\(^24\) This result was interpreted as a consequence of the fully thermal nature of the desorption process.

In the present investigation, we again examine the isotope effect for simple molecular desorption, in a system where an electronic desorption mechanism is known to be operative. We have chosen for this purpose \( \text{O}_2/\text{Pd}(111) \), for which femtosecond laser-induced surface processes have been extensively investigated\(^14,19\) and for which complementary studies of thermal chemistry\(^26–29\) and conventional photochemistry\(^30–35\) provide valuable points of reference. For this system, we find a strong isotope effect of \( 1.8 \pm 0.3 \) in the relative yield of femtosecond laser-induced desorption (LID) for \( ^{16}\text{O}_2 \) compared with \( ^{18}\text{O}_2 \). In this work, we report the results and procedure for this experiment. We consider the implications of the findings for adsorbate/substrate coupling and the mechanism of the femtosecond desorption process on a qualitative level. We find that the results are incompatible with full equilibrium between the adsorbate and the substrate, whether at the lattice or electronic temperature. They can be understood in terms of a mechanism driven by the high substrate electronic temperature, but with excitation in the desorption coordinate of the adsorbate only coming into partial equilibrium with the substrate electrons.

\(^{a}\)Also at Department of Electrical Engineering, Columbia University, New York, NY 10027; electronic mail: tony.heinz@columbia.edu
II. EXPERIMENT

The experiments were conducted using an ultrahigh vacuum system with a base pressure below $10^{-10}$ Torr. The single-crystal Pd(111) surface was cleaned by means of argon-ion sputtering at 0.5 kV followed by annealing to 900 K. A chemical cleaning process was also employed in which the Pd sample was annealed in a relatively high partial pressure of oxygen gas ($10^{-8}$ Torr). This step was effective in reducing carbon and sulfur contamination through oxidation of the surface species. The purity of the sample surface was checked by means of Auger electron spectroscopy, and the ordering of the Pd(111) lattice was verified using low-energy electron diffraction. Since the carbon Auger peak is largely obscured by a Pd feature, we checked for carbon contamination by looking for volatile reaction products. This was accomplished by exposing the surface to oxygen and measuring desorbed CO and CO$_2$ in temperature programmed desorption (TPD) spectra with a quadrupole mass spectrometer (QMS).

The laser source was based on a Kerr-lens mode-locked Ti:sapphire oscillator, which was amplified in a regenerative amplifier and produced pulses at a repetition rate of 1 kHz and a center wavelength of 810 nm. The pulse duration during the experiments was approximately 300 fs at the surface and the energy per pulse was adjustable up to a value of 600 µJ. For the experimental measurements, the laser beam was incident on the sample at an angle of incidence of 30° and was $p$ polarized. The beam illuminated a region of approximately 1 mm diameter on the sample and was arranged to yield an absorbed fluence of approximately 25 J/m$^2$ near the center of the beam. This figure was deduced using a charge coupled device (CCD) camera to provide a two-dimensional image of the spatial profile of the laser beam at a distance equivalent to the sample, in conjunction with a careful measurement of the total pulse fluence.

During the experiments, the substrate was held at a base temperature of 95 K and was exposed to saturation dosing of oxygen using a capillary array doser. The sample temperature was measured with a thermocouple spot welded to the back of the sample. The quality of the sample surface and the adsorbate coverage were examined through measurement of TPD spectra, as shown in Fig. 1. They revealed the $\alpha_1$, $\alpha_2$, and $\alpha_3$ peaks expected for molecular desorption from the saturated surface. The states are labeled in order of their binding energy, $\alpha_1$ being bound the most strongly. At high surface temperatures, the $\beta$ peak from recombinative desorption was also observed (see Fig. 1). Its strength is a sensitive measure of the cleanliness of the surface, particularly with respect to carbon contamination, and provided a further check of sample cleanliness. When dosing with either the pure $^{16}$O$_2$ or $^{18}$O$_2$ isotope, we did not observe more than trace levels of the opposite (or mixed) oxygen isotope in any of the TPD measurements. Contamination levels were compatible with the 97% purity of the commercially supplied $^{16}$O$_2$ feed gas. We also prepared a surface with a mixed monolayer of the two isotopic species by dosing with a gas containing a suitable admixture of the two isotopic species.

Figure 1 shows a multiplexed TPD scan for the mixed monolayer. The molecular TPD features were similar to those of each of the separate isotopic species. Statistical mixing of $^{16}$O and $^{18}$O was also observed for the recombinative peak, although with a relative intensity favoring the $^{16}$O isotope. The origin of this effect is unknown, but is attributed to intermixing with subsurface oxygen, which is dominated by the more common light isotope.

For the LID measurements, the sample was brought into close proximity with the QMS. The relative yield for desorption induced by a single laser pulse was obtained by integration of the transient electrical pulse measured by the QMS. The typical yield per laser pulse was approximately $3 \times 10^{-7}$ monolayer (ML). In these measurements, the 1 kHz repetition rate was too high to permit convenient recording of the transients on the QMS. Consequently, we needed to lower the repetition rate of the laser source. To optimize stability, this was done by optical selection of the pulses with the amplified laser system continuing to operate at its usual 1 kHz repetition rate.

III. RESULTS

Table I shows the results of a preliminary LID measurement with the Pd(111) surface dosed separately by the two pure isotopic species of O$_2$. The measurements were undertaken to verify the correctness of the procedure and the integrity of the experimental data. As can be seen in Table I, when the sample was dosed with $^{16}$O$_2$, both the TPD and LID signals were present only for $^{16}$O$_2$, without any significant $^{18}$O$_2$ contaminant. Correspondingly, when the sample was dosed with $^{18}$O$_2$, only trace $^{16}$O$_2$ signals were observed.
The data, all recorded for an absorbed fluence of approxi-
layer as a function of the number of consecutive laser pulses.

Table I. Yields for saturation doses of specific $^{16}\text{O}_2$ and $^{18}\text{O}_2$ isotopes of
molecular oxygen adsorbed on the Pd(111) surface. The TPD data represent
the relative yields of the molecular desorption peaks during temperature-
programmed desorption; the LID data indicate the yields from femtosecond
laser-induced desorption. The results show that no appreciable contamina-
tion of the isotopic species occurs during the measurements.

<table>
<thead>
<tr>
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<th>Dose $^{16}\text{O}_2$</th>
<th>Dose $^{18}\text{O}_2$</th>
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<tr>
<td>TPD</td>
<td>$^{16}\text{O}_2$</td>
<td>100</td>
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<tr>
<td></td>
<td>$^{18}\text{O}_2$</td>
<td>0</td>
</tr>
<tr>
<td>LID</td>
<td>$^{16}\text{O}_2$</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>$^{18}\text{O}_2$</td>
<td>0</td>
</tr>
</tbody>
</table>

The primary experimental results are displayed in Fig. 2.
Shown in the lower part of Fig. 2 are plots of the $^{16}\text{O}_2$ and
$^{18}\text{O}_2$ yield for LID from the coadsorbed $^{16}\text{O}_2+^{18}\text{O}_2$ mono-
layer as a function of the number of consecutive laser pulses.
The data, all recorded for an absorbed fluence of approxi-
mately 25 J/m², were recorded by measuring alternately the
QMS signal for each isotope in successive laser pulses. The
fall off in the yield reflects the depletion of the adsorbed
molecules. The data points correspond to an average over six
separate experimental runs. For each run, the data are nor-
malized to correct for any slight departure from the nominal
50–50 admixture of the two isotopes in the initial state.
Since the area in which LID occurred was a very small frac-
tion of the total sample area (<1%), we were able to obtain
this correction factor for the actual experimental surface condi-
tion by recording a TPD spectrum after each LID measure-
ment was complete. Although fluctuations in the individual
sets of data were large, no systematic variation was observed
in the different corrected data sets.

The decay of the signal for each isotope reflects depletion
of the corresponding species on the surface. Each signal
drops to a negligible yield upon application of a sufficient
number of laser pulses. As just indicated, only the oxygen in
a small portion of the sample, corresponding to the area ex-
posed by the laser beam, is depleted. In a separate experi-
ment, however, the laser beam was thoroughly rastered over
the entire sample. A TPD measurement was then performed.
In this fashion, we verified that repeated exposure to the laser
pulses leads to the complete depletion of the adsorbed oxy-
gen, as reported earlier for the $^{16}\text{O}_2$ species. 19 Also in agree-
ment with the earlier study, 19 we found no evidence for laser-
induced dissociation of the adsorbed oxygen. We observed
neither a substantial atomic oxygen signal in the QMS during
laser exposure nor the presence of a recombinative desorp-
tion peak in the TPD measurements after thorough rastering
of the sample. Thus, we conclude that the exposure of the
femtosecond laser leads solely and fully to the desorption of
the molecular oxygen.

In order to compare the efficiency of desorption for the
two isotopes, we fit the experimental decay data to an an-
alytic function. For this purpose, we adopted a double-
exponential decay function, which, as shown in the lower
panel of Fig. 2, provides a good description of the experi-
mental observation. The choice of the double-exponential
form reflects the fact that two binding sites are present for
the saturated O$_2$/Pd(111) system in this temperature range.
They correspond to the singly charged superoxo ($\alpha_1$) and
doubly charged peroxo binding sites of O$_2$. Repulsive
adsorbate–adsorbate interactions associated with their charge
are believed to cause the peroxo state to be observed as two
distinct TPD features 29 (labeled $\alpha_1$ and $\alpha_2$). At higher sur-
face coverage, the adsorbate–adsorbate interactions cause
the peroxo species to be bound more weakly, corresponding to
the $\alpha_2$ state; as the coverage decreases, the effective bind-
ing energy increases, yielding the $\alpha_1$ feature. This subtlety is
not, however, reflected in the biexponential function, where
one decay is associated with the superoxo and one decay
with the peroxo species. A more detailed analysis of the LID
yield as a function of the laser exposure would undoubtedly
yield a departure from the simple biexponential form. How-
ever, since our primary emphasis is on the desorption behav-
or near saturation coverage, we have not pursued this issue.

In the upper part of Fig. 2, we display the ratio $R$
$=Y^{(18)}/Y^{(16)}$ of the $^{18}\text{O}_2$ to the $^{16}\text{O}_2$ LID yield computed
from the fits to the decay curve of $^{18}\text{O}_2$ and $^{16}\text{O}_2$. The sim-
pllest regime to interpret is that of the initial phase, before substantial adsorbate depletion has occurred. Here the primary contribution to the signal is understood to be from desorption from the weaker binding site, the superoxo $\alpha_3$ state. For the initial part of the measurement from the undepleted surface, we find a value of $R_0 = Y_0^{(16)}/Y_0^{(18)} = 1.8 \pm 0.3$. The error bar has been calculated by consideration of the uncertainty in the two fitting curves. The isotope ratio $R$ clearly changes as the monolayer is depleted. A drop is, in fact, expected simply as a consequence of the unequal desorption rate of the two isotopes: The $^{16}$O$_2$ species is depleted from the surface more rapidly than the $^{18}$O$_2$ species. Consequently, the desorption yield for $^{16}$O$_2$ will fall off more rapidly than that of the $^{18}$O$_2$, and the ratio $R = Y^{(16)}/Y^{(18)}$ will decrease. The picture is complicated by the presence of the $\alpha_1/\alpha_2$ (peroxo) adsorption state of the adsorbed oxygen molecules. The intrinsic ratio of the isotopic yields for this state may differ from that of the $\alpha_3$ state which, because of its lower binding energy, is presumed to dominate the desorption on the saturated surface. The observed trend of a decreasing isotope effect with increasing adsorbate depletion would, however, still be expected.

IV. DISCUSSION

It is instructive to compare the observed isotope effect with the behavior predicted for the more conventional regimes of desorption. First, for desorption occurring under equilibrium conditions, one would not expect any significant dependence of desorption rate on isotopic mass. This same reasoning would be expected to apply for a rapid transient heating, provided that the relevant adsorbate degrees of freedom remain in full thermal equilibrium with the substrate. Thus, a traditional transient heating scheme can be excluded, based on the result of the present isotope measurement, as a mechanism for desorption under our experimental conditions. This conclusion, of course, has already been drawn in the earlier studies of this system performed under similar conditions.

The other limit in which we can apply existing paradigms to discuss the isotope effect is that of a single-excitation model, corresponding to conventional electron- and photon-stimulated desorption via a DIET process. The familiar analysis considers a semiclassical model in which adsorbates are promoted to an excited state. While the adsorbate is in an excited state, it gains kinetic energy before returning to its ground state. Upon returning to the ground state, the adsorbate may either desorb or remain trapped, depending on the amount of energy gained during the transient electronic excitation. In such a DIET process, an isotope effect is predicted in the following way: Since the excited-state lifetime is the same for two isotopes, the lighter one gains more kinetic energy as it traverses the common potential energy surface. It thus has a higher chance of desorbing upon de-excitation. In the limit of low desorption probability relevant for chemisorbed molecules on metals (with short excited-state lifetimes), the small effect of the isotopic mass on the Newtonian dynamics of the adsorbate can lead to a significant effect in the relative desorption yield. As presented in the earlier work of Leung et al., the isotopic ratio for desorption efficiency $R$ is given by

$$\frac{\sigma_1}{\sigma_2} = \left( \frac{1}{P_1} \right)^{m_2/m_1-1} \frac{m_1}{m_2} \frac{S_1}{S_2}.$$  

Here $m_1$ and $m_2$ are the masses of the isotopes in question, and $\sigma_1$ and $\sigma_2$ are, respectively, their desorption cross sections. $P_1$ is the probability that the isotope of mass $m_1$ will desorb upon excitation: For an excitation cross section $\sigma_1^{(ex)}$, the desorption cross section is given by $P_1$, through the formula $\sigma_1 = \sigma_1^{(ex)} P_1$. These relations have been employed in a variety of earlier experiments carried out with conventional excitation.

If we apply this treatment to our current experimental result of $R_0 = 1.8$, we deduce a value of $P_1 \sim 6 \times 10^{-5}$. Such a very low desorption probability $P_1$ upon excitation is not unreasonable for chemisorbed molecules on a metal surface, since excited-state lifetimes are frequently as short as a few femtoseconds. Thus, this analysis can account for the observed isotope effect. We regard this discussion, however, more as illustrative of the role of nonequilibrium excitation than as a proper description of our experimental results. It indicates that for strongly nonequilibrium conditions, a large isotope effect can occur. A more detailed consideration of the current experiment must recognize that under the conditions of intense femtosecond laser excitation, we produce a high density of excited electrons. A mechanism involving the excitation of the adsorbate by a single photon (mediated through a substrate electron–hole pair), as in the conventional regime, is incompatible with the observed nonlinear fluence dependence of the desorption yield. We may also note that the analysis of the isotope effect just presented is also inconsistent with the behavior of a conventional DIET process. If we combine the inferred value for the desorption probability after excitation of $P_1 \sim 6 \times 10^{-5}$ with the experimental value for the adsorbed photon flux (≈ $1.0 \times 10^{20}$ m$^{-2}$ s$^{-1}$) and the measured desorption yield (≈ 0.003 ML/pulse), we infer an effective cross section for excitation of $170 \AA^2$ for each absorbed photon. This value appears to be unphysically large. It indicates the inadequacy of a picture of desorption based on activation by single electron–hole pairs produced in the metal. As has been extensively discussed in the literature, the distinctive characteristics of the femtosecond desorption process can, however, be understood in terms of the high electronic temperature induced in the substrate and the coupling of this transient electronic excitation to motion of the adsorbate.

In a separate work, we examine the isotope effect in the context of a model of desorption based on transient electron heating. Under the conditions of our experiment, we find that the substrate electrons achieve a temperature approaching 2000 K for a period of a few picoseconds before cooling by coupling to the substrate phonons and by diffusion into the bulk of the material. Heating of the phonon degree of freedom is relatively modest because of its substantially greater heat capacity compared with that of the substrate.
electrons. As indicated by the high desorption yield, as well as the duration of previously reported two-pulse correlation measurements, it is this electronic temperature transient that is responsible for desorption of the oxygen molecules.\textsuperscript{14}

Within this context, the large observed isotope effect cannot be explained by full equilibration of motion of the adsorbate in the desorption coordinate and the substrate electronic degree of freedom. Suppose, on the other hand, that the adsorbate excitation in the desorption coordinate is still driven by the electronic temperature transient, but only achieves partial equilibration during the course of the rapid temperature transient. In this case, a strong isotope effect may be expected. In our analysis,\textsuperscript{36} we treat this situation by assuming adsorbate/substrate coupling through an electronic friction.\textsuperscript{37,38} Within this treatment, the isotopic dependence arises from the known dependence of the electronic friction on the adsorbate mass.\textsuperscript{38} We are then able to reproduce, at a semi-quantitative level, the isotope effect reported here. The analysis reveals that the adsorbate temperature appreciably lags the substrate electronic temperature, corresponding to a significant departure from an equilibrium process at the substrate electronic temperature.

In conclusion, we have reported an isotope effect for femtosecond LID in the coadsorbed system of $^{16}\text{O}_2$/$^{18}\text{O}_2$/Pd(111). We find a ratio of the desorption yields of $R_0 = \frac{Y_{16}}{Y_{18}} = 1.8 \pm 0.3$ for a saturated surface at a base temperature of 95 K. Such a strong isotope effect cannot be understood within a conventional thermal model of desorption. Comparable isotope effects have previously been associated with the highly nonequilibrium process of DIET, but, as reported here, are clearly also observable for a desorption process in the regime of elevated electronic temperature. The isotope effect reflects the lack of full equilibration between the high substrate electronic temperature driving the desorption process and the motion of molecules along the desorption coordinate.

**ACKNOWLEDGMENT**

The authors gratefully acknowledge support from the Petroleum Research Foundation.

\textsuperscript{36}D. P. Quinn and T. F. Heinz (unpublished).