

# Surface photochemistry induced by ultrafast pulses of vacuum ultraviolet light: Physisorbed oxygen on graphite

D. Riedel,\* L. M. A. Perdigão, J. L. Hernández-Pozos,† Q. Guo, and R. E. Palmer‡

*Nanoscale Physics Research Laboratory, School of Physics and Astronomy, The University of Birmingham, Edgbaston, Birmingham B15 2TT, United Kingdom*

J. S. Foord

*Physical and Theoretical Chemistry Laboratory, The University of Oxford, South Parks Road, Oxford, South Parks Road, Oxford OX1 3QZ, United Kingdom*

K. W. Kolasinski§

*School of Chemistry, The University of Birmingham, Edgbaston, Birmingham B15 2TT, United Kingdom*

(Received 24 September 2002; published 17 December 2002)

We report a surface photochemistry study using ultrafast pulses of vacuum ultraviolet (vuv) light for excitation. Tunable vuv radiation (10–38 eV) is produced via high harmonic generation. We have studied the model system of physisorbed  $O_2$  on graphite. The only observed desorption product is  $O^+$ , the yield of which is measured as a function of the excitation photon energy. The kinetic energies of the desorbed ions are obtained by time-of-flight measurements with the pulsed source. These measurements enable us to suggest that the  $O^+$  desorption proceeds through more than one channel and to identify the electronic transitions that may be involved in the dissociative ionization of the physisorbed  $O_2$ .

DOI: 10.1103/PhysRevB.66.233405

PACS number(s): 82.50.Hp, 33.80.Gj, 78.47.+p, 79.20.La

Surface photochemistry is important in a wide range of fields from interstellar chemistry<sup>1,2</sup> to semiconductor processing.<sup>3,4</sup> Adsorbed molecular oxygen, in particular, has served as a prototypical system, the study of which has led to a number of advances in our understanding of surface photochemistry. Most of these studies have concentrated on photochemistry induced by low-energy photons (infrared, visible, and near ultraviolet) on metal<sup>5–11</sup> and semiconductor surfaces.<sup>12–15</sup> Ultrafast laser excitation of  $O_2$  on Pd led to the first observation of dissociation induced by multiple excitations.<sup>16</sup> The role of electron capture (negative-ion resonance formation<sup>17</sup>) in the photochemistry of  $O_2$  has also been explored.<sup>18</sup> Nanosecond and femtosecond excitations have been used to initiate photochemical reactions between coadsorbed  $O_2$  and CO to form  $CO_2$ ,<sup>19–24</sup> leading to subsequent single-molecule experiments with the scanning tunneling microscope.<sup>25</sup>

The photochemistry induced by vacuum ultraviolet (vuv) photons is of particular interest because vuv photons can excite a range of different molecular electronic states, which may exhibit specific resonant behavior.<sup>26,27</sup> The dynamics of the electronic states of the free  $O_2$  molecule are well known from gas-phase studies,<sup>28–31</sup> and comparisons with the adsorbed phase lead to insights into the effects of adsorption on electronic structure and dynamics. It is also of interest to compare the vuv photochemistry of physisorbed  $O_2$  to that of chemisorbed  $O_2$ , such as  $O_2$  chemisorbed on Si(111)-(7 × 7).<sup>27</sup> Previous synchrotron-based studies<sup>32–35</sup> of physisorbed  $O_2$  on graphite have revealed interesting new dynamics that appear to be operative only at higher photon energies. Adsorbed  $O_2$  has also been involved in the first study to use high harmonic generation (HHG) to follow the course of a photochemical reaction.<sup>36</sup> In that study, vuv photons produced by HHG were used to *probe* the infrared-initiated pho-

tochemistry of  $O_2$  chemisorbed on Pt(111) via ultrafast photoemission measurements. HHG has also been employed<sup>37</sup> to probe the ultrafast photodynamics of  $Br_2$  dissociation in the gas phase as well as electron dynamics at surfaces.<sup>38,39</sup>

In this Brief Report, we employ ultrafast vuv pulses to induce surface photochemistry. The vuv source, described elsewhere,<sup>40</sup> is based on HHG in argon or xenon and delivers (after selection with a monochromator)  $\sim 10^{10}$  photons  $s^{-1}$ . Such a source has two principal attractions to initiate reaction dynamics—it is tunable and has a pulse duration on the order of a picosecond. We report the yield of desorbed  $O^+$  ions resulting from the photodissociation of  $O_2$ /graphite excited at 10–38 eV using harmonics 7 to 23 (H7 to H23). For an  $O_2$  coverage of  $\sim 4$  monolayers (ML), we observe the onset of  $O^+$  desorption at  $\sim 17$  eV, a plateau at 19.5–29 eV, and a steep increase in cross section above 29 eV. The ion kinetic energy distributions, derived from time-of-flight (TOF) measurements, permit a discussion of the decay channels that occur for excitation at different photon energies associated with the opening of additional decay channels at high photon energy.

The experiments employed an ultrahigh vacuum (UHV) chamber (base pressure  $< 10^{-10}$  Torr) equipped with a liquid-He cryostat and a mass spectrometer. The sample was cooled to 20–22 K and measured with a rhodium-iron resistance thermometer. Gas dosing [with  $O_2$  (99.998% purity) or CO (99.997% purity)] was performed via a leak valve at a chamber pressure of  $2 \times 10^{-8}$  Torr. For all experiments an exposure of 12 langmuir (1 langmuir =  $10^{-6}$  Torr s) was used, which we believe corresponded to an  $O_2$  coverage just under 4 ML. The leak valve was closed during data acquisition such that experiments were performed in the absence of gas-phase  $O_2$  but at a pressure slightly above the base pres-

sure of the chamber due to the influx of argon or xenon from the HHG source chamber. To minimize this, a series of apertures are used to isolate the source chamber from the UHV chamber. Furthermore, a pulsed valve, working at 1 kHz, was used to decrease the total gas load. The amounts of Ar or Xe detected in the mass spectrometer during vuv irradiation were always negligible in comparison with the ions  $C^+$  or  $O^+$ . A vuv monochromator selected the desired harmonic generated by the HHG process.<sup>40</sup> The monochromator resolution was sufficient to ensure that only the selected harmonic is incident upon the sample while all others were suppressed. A removable scintillator was placed in a differential pumping chamber between the monochromator and UHV chambers to measure the vuv photon flux before it reached the highly oriented pyrolytic graphite sample. The vuv beam direction was adjusted to maintain a constant photon flux on the surface sample. This was determined for all harmonics by measuring the yield of photoelectrons acquired with the mass spectrometer (Hiden). The mass spectrometer was modified to allow TOF measurements in addition to quadrupole mass spectrometry (QMS). The channeltron signal was detected before discrimination with a multichannel analyzer triggered by the laser. To accelerate ions created at the surface by the pulsed vuv irradiation, a dc voltage was applied between the sample and the entrance grid of the mass spectrometer. Detection of desorbed neutrals was not attempted, given the signal levels involved.

Calibration of the mass spectrometer used in TOF mode is key to the identification of the ionic species desorbed. Thus, we collected TOF spectra for ions desorbed from both physisorbed  $O_2$ /graphite and physisorbed CO/graphite. In both cases we observed the desorption of only one positively charged ionic fragment. Variation of the extraction voltage (25, 50, or 100 V) allowed us to identify unambiguously the masses of the ionic fragments and to measure the drift length ( $D = 0.2731 \pm 0.0009$  m). The only ionic fragment observed to desorb from  $\sim 4$  ML films of  $O_2$  on graphite held at 20 K (for all photon energies) was  $O^+$ . Only  $C^+$  ions were detected from  $\sim 4$  ML CO/graphite at 20 K for excitation at 32.55 eV.

The tunability of the HHG source allowed us to measure the  $O^+$ -ion yield from physisorbed  $O_2$  ( $\sim 4$  ML) as a function of photon energy. Each experimental point represents the signal accumulated in 15 min, as shown in Fig. 1. The main features apparent in Fig. 1 are (i) a slow rise in the  $O^+$  signal out of the background noise with an estimated appearance threshold of  $17 \pm 1$  eV, (ii) a plateau region where the yield is relatively constant to at least 26 eV, and (iii) a further steep increase in the yield above 29 eV. The yield of  $O^+$  measured for physisorbed  $O_2$  differs markedly from the yield of  $O^+$  from chemisorbed  $O_2$ . For the latter case, Dujardin *et al.*<sup>27</sup> recorded a monotonically increasing  $O^+$  desorption signal with a threshold at 33 eV.

The time structure of our vuv pulses allowed us to measure readily kinetic energy distributions and the concomitant additional dynamical information. Furthermore, since the photon energy is also tunable, we were able to make these measurements as a function of excitation energy. We made such measurements with both H15 (23.25 eV) and H21

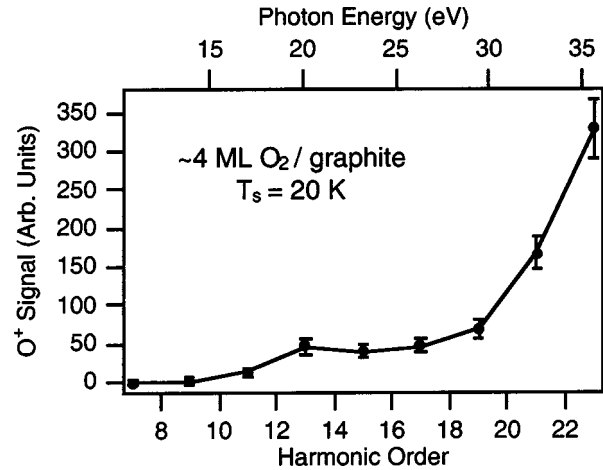


FIG. 1. Measurement of the  $O^+$ -ion yield as a function of the photon energy generated by the high harmonic vacuum ultraviolet source for a coverage of  $\sim 4$  ML of  $O_2$ /graphite at 20 K. The ion acceleration voltage to the time-of-flight detector was 100 V.

(32.55 eV). From the calibrated total flight distance, we were able to determine the initial kinetic energy of the  $O^+$  ion,  $E_K$ , as it left the surface, from the following equation:<sup>41</sup>

$$E_K = \frac{mD^2}{2t^2} - eV. \quad (1)$$

Here,  $m$  is the mass of the ion,  $D$  is the drift length,  $t$  is the measured flight time, and  $eV$  is the kinetic energy acquired by the ion of charge  $e$  in the acceleration region. In Figs. 2

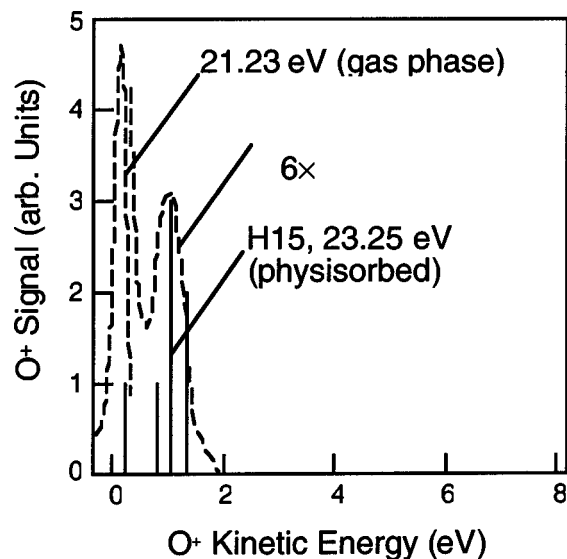


FIG. 2. Comparison of the kinetic energy distributions of photo-desorbed  $O^+$  ions from  $\sim 4$  ML of  $O_2$ /graphite at 20 K excited at H15 ( $h\nu = 23.25$  eV). Also plotted is the gas-phase dissociative photoionization data at  $h\nu = 21.23$  eV from Ref. 28.

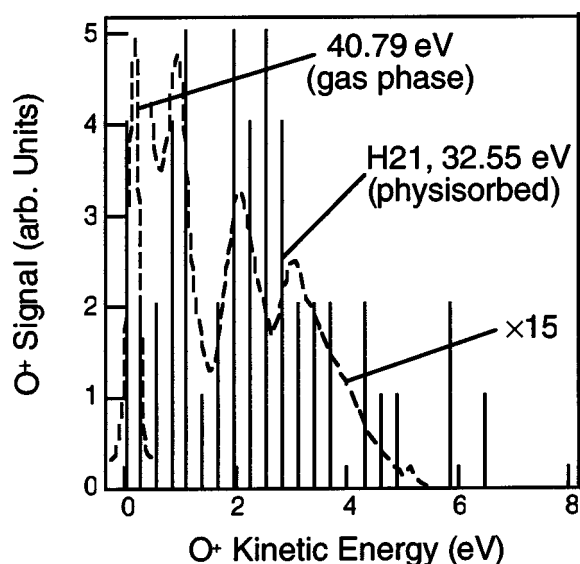


FIG. 3. Comparison of the kinetic energy distributions of photodesorbed  $O^+$  ions from  $\sim 4$  ML of  $O_2$ /graphite at 20 K excited at H15 ( $h\nu = 32.55$  eV). Also plotted is the gas-phase dissociative photoionization data at  $h\nu = 40.79$  eV from Ref. 28.

and 3, the TOF data have been transformed into kinetic energy distributions (KED) for the two photon energies. Corresponding gas-phase data<sup>28</sup> at similar photon energies are overlaid for comparison. These KED's allow us to hone in on the mechanisms of surface photodynamics in a way that is not possible from the yield measurements alone.

For excitation at 23.25 eV, Fig. 2, the kinetic energy distribution consists of one peak at  $\sim 1$  eV. Excitation at 32.55 eV, Fig. 3, leads not only to the 1-eV peak but also to significant broadening on the high-energy side of the distribution. There is also significant signal near  $E_K = 0$  eV in the latter case. Within our signal-to-noise ratio, the KED's are remarkably similar to the KED's reported by, e.g., Gardner and Samson<sup>28</sup> and Lu *et al.*<sup>31</sup> for dissociative photoionization of gas-phase  $O_2$ . The similarity between the gas- and adsorbed-phase distributions pertains to the breadth of the KED's; however, the magnitudes of the features within the distributions differ significantly. In particular, the peak near  $E_K = 0$  in the gas phase is greatly reduced in the surface experiments. This observation is consistent with the idea that ions created with less than a certain critical  $E_K$  will be recaptured by the polarization potential at the surface. Significantly, in gas-phase photodissociation of  $O_2$ , at least 90% of the fragmentation events lead to  $O^+$  with near zero kinetic energy.<sup>28,31</sup> Since these ions are incapable of escaping from an adsorbed layer we should not expect the  $O^+$  yield versus photon energy to be the same for the adsorbed phase compared with the gas phase *even if dissociative photoionization is governed by essentially the same dynamics at the molecular level in both cases.*

From the similarity of the kinetic energy distributions measured in the gas and adsorbed phases, we conclude that the dissociative photoionization dynamics in the physisorbed

layer is substantially governed by the same molecular dynamical pathways as those observed in the gas phase. Previous studies utilizing synchrotron radiation could not conclusively determine whether direct or substrate-mediated excitation was occurring.<sup>32,35</sup> In the photon energy region from 17 to 22 eV, i.e., 0–5 eV above threshold, the excitation of the physisorbed  $O_2$  must be direct (as opposed to substrate mediated), since photoelectrons produced in this region do not have sufficient energy to initiate dissociative ionization and thus desorb  $O^+$  ions. In the gas phase, high kinetic energy  $O^+$  channels begin to participate appreciably at photon energies  $> 26$  eV. Therefore, the production of  $O^+$  at 32.55-eV excitation may in principle arise either from direct or substrate-mediated processes. Significant changes in the ion yields compared with the gas phase are apparent; in particular, the lowest  $E_K$  features are at least partially suppressed and, in consequence, the higher  $E_K$  features are relatively enhanced. In contrast, the dissociation dynamics of physisorbed  $O_2$  differs significantly from the dynamics of chemisorbed  $O_2$ . This fact is related either to a change in the excitation probability or, perhaps more importantly, to a change in the excited-state relaxation dynamics in the physisorbed versus the chemisorbed state.

Lafosse *et al.*<sup>30</sup> have identified 12 mechanisms for dissociative photoionization of free  $O_2$  in the range 20–28 eV. A two-step process describes the dynamics. First, the molecular ion and a photoelectron are created. Second, the  $O_2^+$  dissociates and the energy of the molecular ion in excess of the dissociation energy is partitioned equally between the O atom and the  $O^+$  ion. Drawing on the work of Lafosse *et al.* and Lu *et al.*,<sup>31</sup> we surmise that for excitation at 23.25 eV, the primary photoinduced ion desorption mechanism is excitation to the  $O_2^+(B^2\Sigma_g^-)$  state followed by fragmentation into the first dissociation limit,  $O^+(^4S) + O(^3P)$ . This process leads to  $O^+$  ions with a kinetic energy centered at  $\sim 1$  eV, consistent with the data in Fig. 3 for excitation at 23.25 eV and corresponding also to the 1-eV peak observed for excitation at 32.55 eV. At 32.55-eV excitation, two additional channels become available, both proceeding via  $O_2^+(c^4\Sigma_u^-)$  and both leading to high kinetic energy  $O^+$  ions ( $\geq 2$  eV). One channel couples to the first dissociation limit, whereas the other couples to the second dissociation limit,  $O^+(^4S) + O(^1D)$ . All other channels lead to the production of low or near-zero kinetic energy  $O^+$  and therefore make a less significant contribution to the KED's we measure. The accessibility of the additional channels, particularly the high-energy ones, correlates with the increased photodesorption cross section. We can exclude the desorption of  $O_2^+$  followed by gas-phase dissociation of the molecular ion, for if this were to occur, the  $E_K = 0$  peak would be the most prominent feature in the KED.

$O_2$ /graphite has a rich phase diagram of structures in the monolayer and multilayer regime that display different adsorbate orientations. In the multilayer phase studied here,  $O_2$  is oriented roughly along the surface normal.<sup>42</sup> Extension of these experiments to other coverages, molecular phases, and to different systems would certainly be of interest. Detection

sensitivity improvements might also allow for the detection of desorbed negative ions. In any event, the  $E_K$  measurements facilitated by the pulsed nature of a laboratory-based, tunable HHG source will provide an important new tool in the elucidation of photochemical dynamics in the vuv region of the spectrum.

The Engineering and Physical Sciences Research Council (U.K.), Subprograma Ciência e Tecnologia do 2nd Quadro Comunitário de Apoio (Portugal) and the European Union have provided financial support for the research program. D.R. also acknowledges the Marie Curie Program of the European Union.

\*Current address: Laboratoire de Photophysique Moléculaire, Université Paris Sud 91405 Orsay, France.

†Current address: Laboratorio de Optica Cuantica, Depto de Fisica, Universidad Autonoma Metropolitana-Iztapalapa, Apdo. Postal 55 534, Mexico D.F, Mexico.

‡Corresponding author: R.E.Palmer@bham.ac.uk

§Current address: Department of Chemistry, Queen Mary, University of London, Mile End Road, London E1 4NS, U.K.

<sup>1</sup>D. P. Ruffle and E. Herbst, *Mon. Not. R. Astron. Soc.* **322**, 770 (2000).

<sup>2</sup>K. Willacy and W. D. Langer, *Astrophys. J.* **544**, 903 (2000).

<sup>3</sup>R. M. Osgood and T. F. Deutsch, *Science* **227**, 709 (1985).

<sup>4</sup>G. M. Wallraff and W. D. Hinsberg, *Chem. Rev.* **99**, 1801 (1999).

<sup>5</sup>L. Hanley, X. Guo, and J. T. Yates, Jr., *J. Chem. Phys.* **91**, 7220 (1989).

<sup>6</sup>A. W. E. Chan, R. Hoffmann, and W. Ho, *Langmuir* **8**, 1111 (1992).

<sup>7</sup>N. Ohta, Y. Ohno, and T. Matsushima, *Surf. Sci.* **276**, L1 (1992).

<sup>8</sup>E. Hasselbrink, H. Hirayama, A. de Meijere, F. Weik, M. Wolf, and G. Ertl, *Surf. Sci.* **269/270**, 235 (1992).

<sup>9</sup>A. de Meijere, H. Hirayama, and E. Hasselbrink, *Phys. Rev. Lett.* **70**, 1147 (1992).

<sup>10</sup>F. Weik, A. de Meijere, and E. Hasselbrink, *J. Chem. Phys.* **99**, 682 (1993).

<sup>11</sup>B. Hellsing and V. P. Zhdanov, *Chem. Phys. Lett.* **226**, 331 (1994).

<sup>12</sup>K. A. Bertness, W. G. Petro, J. A. Silberman, D. J. Friedman, and W. E. Spicer, *J. Vac. Sci. Technol. A* **3**, 1464 (1985).

<sup>13</sup>C. F. Yu, M. T. Schmidt, D. V. Podlensnik, E. S. Yang, and R. M. J. Osgood, *J. Vac. Sci. Technol. A* **6**, 754 (1988).

<sup>14</sup>Y. Chen, J. M. Seo, F. Stepniak, and J. H. Weaver, *J. Chem. Phys.* **95**, 8442 (1991).

<sup>15</sup>D. Gorelik and G. Haase, *J. Phys. Chem. B* **104**, 2575 (2000).

<sup>16</sup>J. A. Misewich, S. Nakabayashi, P. Weigand, M. Wolf, and T. F. Heinz, *Surf. Sci.* **363**, 204 (1996).

<sup>17</sup>J. Wilkes, R. E. Palmer and C. L. A. Lamont, *Phys. Rev. Lett.* **83**, 3332 (1999); R. E. Palmer and P. J. Rous, *Rev. Mod. Phys.* **64**, 383 (1992); R. E. Palmer, *Prog. Surf. Sci.* **41**, 51 (1992).

<sup>18</sup>R. E. Palmer, *Surf. Sci.* **309**, 335 (1994); F. Cemic, O. Dippel, E. Hasselbrink, and R. E. Palmer, *J. Chem. Soc., Faraday Trans.* **91**, 3633 (1995).

<sup>19</sup>W. D. Miehler and W. Ho, *J. Chem. Phys.* **91**, 2755 (1989).

<sup>20</sup>F.-J. Kao, D. G. Busch, D. Gomes de Costa, and W. Ho, *Phys. Rev. Lett.* **70**, 4098 (1993).

<sup>21</sup>W. D. Miehler and W. Ho, *J. Chem. Phys.* **99**, 9279 (1993).

<sup>22</sup>S. Deliwala, R. J. Finlay, J. R. Goldman, T. H. Her, W. D. Miehler,

and E. Mazur, *Chem. Phys. Lett.* **242**, 617 (1995).

<sup>23</sup>D. G. Busch and W. Ho, *Phys. Rev. Lett.* **77**, 1338 (1996).

<sup>24</sup>M. Bonn, S. Funk, C. Hess, D. N. Denzler, C. Stampfl, M. Scheffler, M. Wolf, and G. Ertl, *Science* **285**, 1042 (1999).

<sup>25</sup>J. R. Hahn and W. Ho, *Phys. Rev. Lett.* **87**, 166102 (2001).

<sup>26</sup>M. Petracic, P. N. K. Deenapanray, G. Comtet, L. Hellner, G. Dujardin, and B. F. Usher, *Phys. Rev. Lett.* **84**, 2255 (2000).

<sup>27</sup>G. Dujardin, G. Comtet, L. Hellner, T. Hirayama, M. Rose, L. Philippe, and M. J. Besnardramage, *Phys. Rev. Lett.* **73**, 1727 (1994).

<sup>28</sup>J. L. Gardner and J. A. R. Samson, *J. Chem. Phys.* **62**, 4460 (1975).

<sup>29</sup>T. Akahori, Y. Morioka, M. Watanabe, T. Hayaishi, K. Ito, and M. Nakamura, *J. Phys. B* **18**, 2219 (1985).

<sup>30</sup>A. Lafosse, J. C. Brenot, A. V. Golovin, P. M. Guyon, K. Hoejrup, J. C. Houver, M. Lebech, and D. Doweck, *J. Chem. Phys.* **114**, 6605 (2001).

<sup>31</sup>Y. Lu, Z. X. He, J. N. Cutler, S. H. Southworth, W. C. Stolte, and J. A. R. Samson, *J. Electron Spectrosc. Relat. Phenom.* **94**, 135 (1998).

<sup>32</sup>R. A. Bennett, S. L. Bennett, L. Sjöller, M. A. MacDonald, R. E. Palmer, H. M. Wright, and J. S. Foord, *J. Phys.: Condens. Matter* **6**, 1955 (1994).

<sup>33</sup>C. M. Friedrich, J. Wilkes, R. E. Palmer, S. L. Bennett, M. A. MacDonald, C. L. A. Lamont, and J. S. Foord, *Chem. Phys. Lett.* **247**, 348 (1995).

<sup>34</sup>L. Sjöller, S. L. Bennett, M. A. MacDonald, R. A. Bennett, R. E. Palmer, and J. S. Foord, *Phys. Rev. Lett.* **76**, 1960 (1996).

<sup>35</sup>L. Sjöller, S. L. Bennett, H. M. Crabtree, R. A. Bennett, J. Wilkes, C. L. A. Lamont, M. A. MacDonald, R. E. Palmer, and J. S. Foord, *J. Phys.: Condens. Matter* **9**, 5815 (1997).

<sup>36</sup>M. Bauer, C. Lei, K. Read, R. Tobey, J. Gland, M. M. Murnane, and H. C. Kapteyn, *Phys. Rev. Lett.* **87**, 025501 (2001).

<sup>37</sup>L. Nugent-Glandorf, M. Scheer, D. A. Samuels, A. M. Mulhisen, E. R. Grant, X. Yang, V. M. Bierbaum, and S. R. Leone, *Phys. Rev. Lett.* **87**, 193002 (2001).

<sup>38</sup>R. Haight and P. F. Seidler, *Appl. Phys. Lett.* **65**, 517 (1994).

<sup>39</sup>A. Rettenberger and R. Haight, *Surf. Sci.* **414**, 197 (1998).

<sup>40</sup>D. Riedel, J. L. Hernández-Pozos, S. Baggott, K. W. Kolasinski, R. E. Palmer, and J. S. Foord, *Rev. Sci. Instrum.* **72**, 1977 (2001).

<sup>41</sup>R. J. Cotter, *Time-of-Flight Mass Spectrometry* (American Chemical Society, Washington, D.C., 1993).

<sup>42</sup>R. J. Guest, A. Nilsson, O. Björneholm, B. Hernnäs, A. Sandell, R. E. Palmer, and N. Mårtensson, *Surf. Sci.* **269/270**, 432 (1992).