J|A|C|S
COMMUNICATIONS

Photoinduced Abstraction Reactions within NO Dimers on Ag(111)

Ki Hyun Kim,[†] Kazuo Watanabe,*[,†] Dietrich Menzel,[†,‡] and Hans-Joachim Freund[†]

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany, and Physik-Department E20, Technische Universität München, 85748 Garching, Germany

Received November 3, 2008; E-mail: watanabe@fhi-berlin.mpg.de

The NO dimer, $(NO)_2$, has been a focus of both experimental and theoretical investigations because of its very complicated electronic states and photochemical reaction dynamics. These are due to the weak N−N bond between the NO radicals which is intermediate between covalent and van der Waals bonds.[1] Photoexcitation of the gaseous NO dimer with UV photons (~6 eV) leads to photodissociation into NO(X) + NO(A).[1] Photoirradiation of NO dimers adsorbed on cold Cu and Ag surfaces, on the other hand, results in the formation of N_2O + O as well as dissociation into NO + NO already from 2 eV upward. It is accepted that these processes are mediated by hot electrons from the metal substrates.[2] The NO dimer on Ag(111) exists in the *cis*-form, nitrogen-down structure.[3] The N_2O formation may be regarded as an abstraction reaction where one nitrosyl captures the N atom from its counterpart, rather than dissociation of a nitrosyl followed by association of N + NO, as evidenced by the absence of nitrogen adatoms after the photoreactions.[4]

In this communication, we report the photochemical formation of dinitrogen (N_2) in addition to N_2O from NO dimers adsorbed on Ag(111). We will show that translationally hot N_2 is produced directly from an NO dimer via simultaneous rupture of its two N−O bonds followed by formation of a N−N triple bond, not by subsequent dissociation of N_2O photoproducts.

All experiments were performed in a two-level ultrahigh vacuum system (base pressure $<10^{-10}$ Torr) consisting of sample preparation and measurement chambers as described before.[5,6] A liquid-helium cooled Ag(111) sample (1 cm in diameter) cleaned by Ar^+ sputtering was dosed with NO gas at 75 K in order to form a saturated monolayer of NO dimers[3] and then cooled down to 30 K. In separate experiments, the second, third, and fourth harmonics (2.3, 3.5, 4.7 eV) of a nanosecond Nd:YAG laser were directed onto the sample surface at 45° from the surface normal in p-polarization (pulse repetition 10 Hz). The beam fluences were ~1 mJ/cm^2 per pulse which led to sample temperature rises small enough to avoid thermal reactions. The photodesorbed species were detected by a quadrupole mass spectrometer (QMS), and their desorption yields and time-of-flight spectra (flight path 19 cm) were recorded by a multichannel scaler (FAST p7882) for each laser shot. The translational temperature ($T_t = \langle E_t \rangle / 2k_B$, where $\langle E_t \rangle$ is mean translational energy and k_B is the Boltzmann constant) was calculated by fitting of the TOF spectra to a sum of shifted Maxwell−Boltzmann distributions.[7]

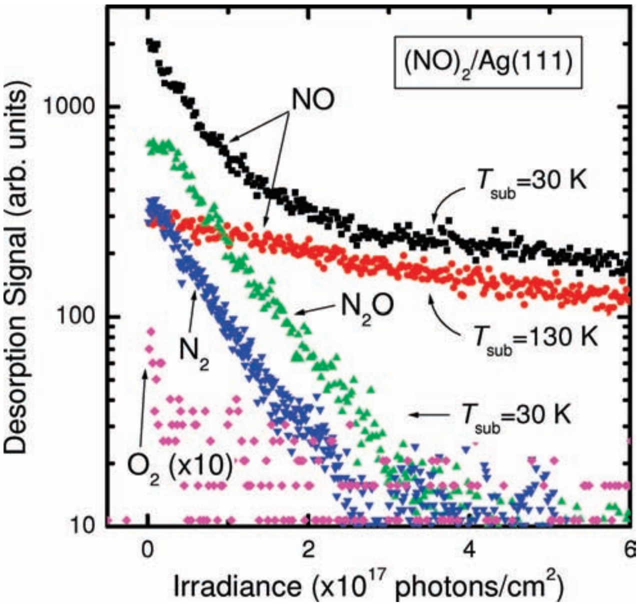

Figure 1. Irradiance dependence of photoinduced desorption (PID) signals of photoproducts of $(NO)_2$ on Ag(111) at 4.7 eV.

Figure 1 displays photoinduced desorption (PID) signals as a function of photon irradiance, i.e., while the initial $(NO)_2$ coverage was converted to products. The signal intensities were corrected by the QMS sensitivities at corresponding mass numbers. The NO signal measured at a substrate temperature (T_{sub}) of 30 K decays initially as the reactant NO dimers are consumed. Later it decays more slowly, when the NO dimers are depleted and photoproduct NO monomers become the main reactant. This is corroborated by the NO signal measured at T_{sub} = 130 K where only NO monomers exist on the surface.[3,4] The slopes of signal decays of N_2O, N_2, and O_2 (T_{sub} = 30 K) are almost the same as that of NO in the early stage. The similarity in decays of the PID signals indicates that these photoproducts are formed from single-photon photoreactions of $(NO)_2$. The initial short plateau seen in the N_2O signal is attributable to the accumulation of photoproduct N_2O on the Ag surface which is depleted by subsequent photoirradiation. A similar PID signal of N_2 from NO adsorbed on Ag(111) at 85 K has been reported before;[2] however, it was ascribed to the fragmentation of photodesorbed N_2O and NO in the QMS. By contrast, the intensity of N_2 signal in Figure 1 is about one-half that of N_2O, which is significantly larger than the cracking pattern of the QMS, and does not exhibit the initial plateau seen in the N_2O signal.

Figure 2 shows the time-of-flight (TOF) spectra of these molecules accumulated for an irradiance of 2 × 10^{18} (2 × 10^{17} for NO) photons/cm^2. One immediately notices that the TOF peak in the N_2 data (Trace A) appears much earlier and is narrower than those of the other species. In contrast, the peak in the TOF spectrum of N_2 photodesorbed from a monolayer of N_2O on Ag(111) at 71 K (Trace B) occurs later and is similar to the shoulder in Trace A. The translational temperature of the fast component of N_2 (the peak in Trace A) is ~5700 K, whereas those of N_2 (Trace B), O_2, N_2O, and NO are 1200, 810, 1200, and 770 K, respectively. We stress that the shapes of TOF spectra of N_2 measured at 2.3 and 3.5 eV

[†] Fritz-Haber-Institut der Max-Planck-Gesellschaft.
[‡] Technische Universität München.

10.1021/ja808615m CCC: $40.75 © 2009 American Chemical Society

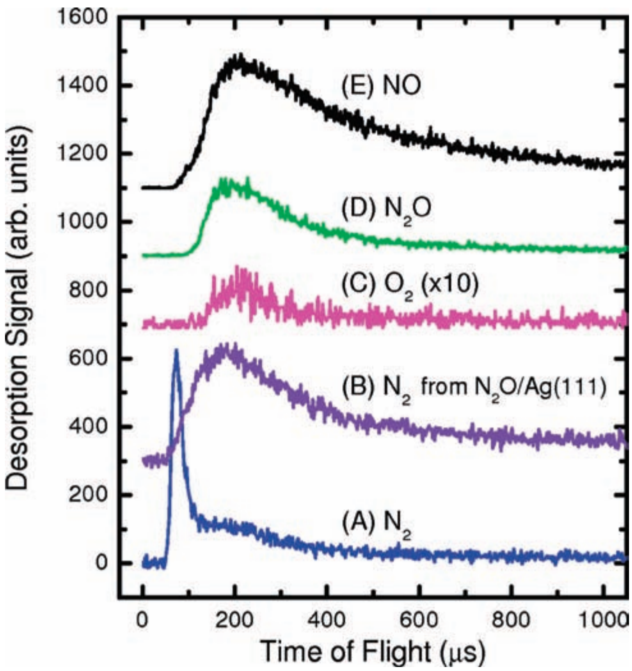

Figure 2. Time-of-flight (TOF) spectra of photoproducts desorbed by 4.7-eV laser irradiation of $(NO)_2$/Ag(111) (Traces A, C−E) and N_2O/Ag(111) (Trace B).

were exactly the same as that of Trace A, though at reduced intensities. This suggests that the N_2 is formed via the same excited states of $(NO)_2$ even at these lower photon energies.

It has been established by previous studies that the photoreactions of $(NO)_2$ on Ag(111) are driven by attachment of hot electrons produced by photoabsorption (>2 eV) in the silver substrate.[2] Theoretical calculations proposed that the affinity level of $(NO)_2$ responsible for photoreaction is located at ~2 eV above the Fermi level.[8] However, the direct photochemical formation of N_2 from $(NO)_2$ has not been identified before, neither on solid surfaces[2] nor in the gas phase.[1]

For the mechanism of the N_2 formation from $(NO)_2$ we suggest the following scenario. The resonance orbital responsible for the photoreactions has antibonding character for both the ON−NO and the N−O bonds.[8] With this orbital being populated by an electron, both the ON−NO and the two N−O bonds will start to elongate. This leads to several possible reaction paths. If the weak ON−NO bond (bond energy 700 cm^{-1})[9] is broken first, two NO molecules desorb; this is the most efficient path as shown by the yields in Figure 1. If one of the N−O bonds is broken earlier than the ON−NO bond, the N atom is abstracted by the other NO and a N−N double bond is formed to produce N_2O (NNO). Finally, if the two N−O bonds split simultaneously and concertedly, the two nitrogen atoms abstract each other to form dinitrogen, N_2. No atomic nitrogen is deposited on the Ag surface, as evidenced by the absence of N_2 formed by its thermal recombination.[4] Theoretical calculations[8,10] show that by adsorption of a free $(NO)_2$ onto Ag(111) its N−N bond is contracted from 2.26 Å to ~1.63 Å, whereas the N−O bond is stretched from 1.15 Å to ~1.21 Å. Thus, the N−N bond formation becomes feasible for the adsorbed $(NO)_2$.

Once N_2 is formed from an adsorbed $(NO)_2$, it finds itself on a very steep repulsive potential since it is too close to the surface. The height of the N atoms in a $(NO)_2$ on Ag(111) is 2.11−2.27 Å,[8] whereas the equilibrium distance between N_2 and Ag(111) is 3.68 Å.[11] The resulting strong repulsion causes the extremely high translational temperature (~5700 K) of the photodesorbed N_2.

As to the split-off oxygen, only a small part photodesorbs by associative recombination to form O_2 (see Trace C of Figures 1 and 2), and only with 3.5- and 4.7-eV irradiation, but not at 2.3 eV. The initial decay of this weak signal is steeper than those of the other products. This indicates that this molecular O_2 signal stems from secondary processes between nascent and/or adsorbed oxygen atoms, $O^* + O^* \rightarrow O_2$ and/or $O^* + O(a) \rightarrow O_2$, and not from a first-order process of the NO dimers, $(NO)_2 \rightarrow N_2 + O_2$. The signal of photodesorbed atomic oxygen (mass 16) was below the detection limit at all the photon energies which could still be due to a detection problem. However, an estimate based on heats of formation shows that the splitting-off of two O atoms from the NO dimers would cost at least 3.4 eV, i.e., is not possible. These results suggest that the majority of oxygen atoms produced by N_2 formation from $(NO)_2$ is adsorbed on the silver surface; some may go subsurface upon heating.

In conclusion, direct photochemical formation of N_2 has been identified for the first time in photoreactions of $(NO)_2$ adsorbed on cold Ag(111), induced by UV and visible light. We propose that this reaction occurs via simultaneous cleavage of the two N−O bonds followed by the formation of a N−N triple bond of N_2 and can be regarded as a mutual abstraction of the N atom from each nitrosyl in $(NO)_2$. The Ag surface reduces the N−N bond length of $(NO)_2$ to enable the formation of N_2 as well as N_2O.

Acknowledgment. We acknowledge financial support from the Deutsche Forschungsgemeinschaft within priority program SPP1093 (Dynamik von Elektronentransferprozessen an Grenzflächen), the German-Israeli Foundation (Dynamics of Electronic Processes in a Confined Environment), the Fonds der Chemischen Industrie, and the NEDO International Joint Research Grant on Photon and Electron Controlled Surface Processes.

References

(1) (a) Gessner, O.; Lee, A. M. D.; Shaffer, J. P.; Reisler, H.; Levchenko, S. V.; Underwood, J. G.; Shi, H.; East, A. L. L.; Wardlaw, D. M.; Chrysostom, E. t. H.; Hayden, C. C.; Stolow, A. *Science* **2006**, *311*, 219. (b) Levchenko, S. V.; Reisler, H.; Krylov, A. I.; Gessner, O.; Stolow, A.; Shi, H.; East, A. L. L. *J. Chem. Phys.* **2006**, *125*, 084301.
(2) (a) So, S. K.; Franchy, R.; Ho, W. *J. Chem. Phys.* **1991**, *95*, 1385. (b) Kidd, R. T.; Lennon, D.; Meech, S. R. *J. Phys. Chem. B* **1999**, *103*, 7480.
(3) Carlisle, C. I.; King, D. A. *J. Phys. Chem. B* **2001**, *105*, 3886.
(4) Vondrak, T.; Burke, D. J.; Meech, S. R. *Chem. Phys. Lett.* **2000**, *327*, 137.
(5) Watanabe, K.; Kim, K. H.; Menzel, D.; Freund, H.-J. *Phys. Rev. Lett.* **2007**, *99*, 225501.
(6) Mulugeta, D.; Kim, K. H.; Watanabe, K.; Menzel, D.; Freund, H.-J. *Phys. Rev. Lett.* **2008**, *101*, 146103.
(7) Zimmermann, F. M.; Ho, W. *Surf. Sci. Rep.* **1995**, *22*, 127.
(8) Nakamura, H.; Yamashita, K. *J. Chem. Phys.* **2006**, *125*, 084708.
(9) (a) Wade, E. A.; Cline, J. I.; Lorenz, K. T.; Hayden, C.; Chandler, D. W. *J. Chem. Phys.* **2002**, *116*, 4755. (b) Hetzler, R.; Casassa, M. P.; King, D. S. *J. Phys. Chem.* **1991**, *95*, 8086. (c) Potter, A. B.; Dribinski, V.; Demyanenko, A. V.; Reisler, H. *J. Chem. Phys.* **2003**, *119*, 7197.
(10) McKellar, A. R. W.; Watson, J. K. G.; Howard, B. J. *Mol. Phys.* **1995**, *86*, 273.
(11) Vidali, G.; Ihm, G.; Kim, H.-Y.; Cole, M. W. *Surf. Sci. Rep.* **1991**, *12*, 135.

JA808615M