

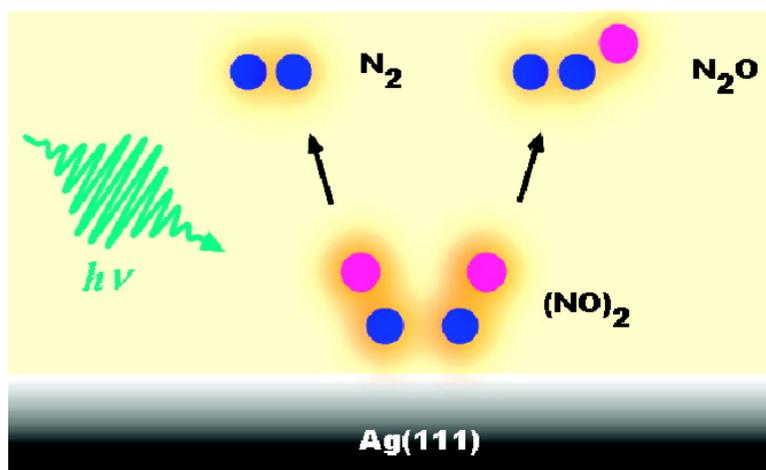
Communication

Photoinduced Abstraction Reactions within NO Dimers on Ag(111)

Ki Hyun Kim, Kazuo Watanabe, Dietrich Menzel, and Hans-Joachim Freund

J. Am. Chem. Soc., **2009**, 131 (5), 1660-1661 • DOI: 10.1021/ja808615m • Publication Date (Web): 15 January 2009

Downloaded from <http://pubs.acs.org> on May 13, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)

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 N₂O + 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 N₂O 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 (N₂) in addition to N₂O from NO dimers adsorbed on Ag(111). We will show that translationally hot N₂ 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 N₂O 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 dimers³ 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/cm² 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 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

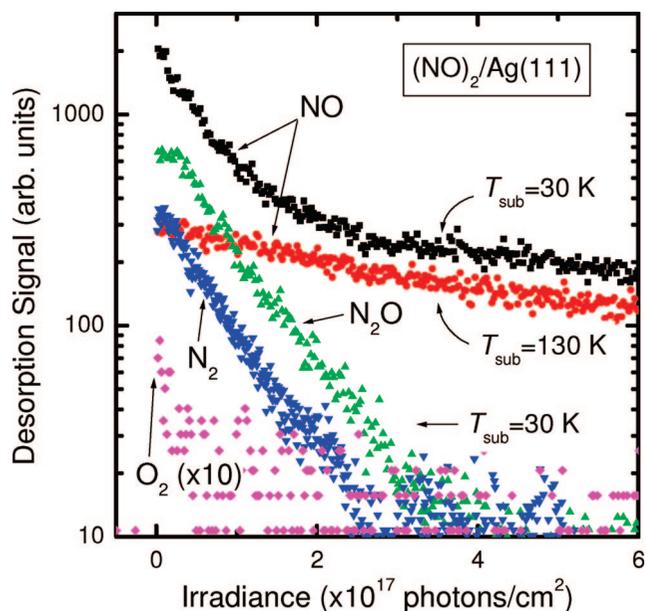


Figure 1. Irradiance dependence of photoinduced desorption (PID) signals of photoproducts of (NO)₂ on Ag(111) at 4.7 eV.

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 $T_{\text{sub}} = 130$ K where only NO monomers exist on the surface.^{3,4} The slopes of signal decays of N₂O, N₂, and O₂ ($T_{\text{sub}} = 30$ 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 N₂O signal is attributable to the accumulation of photoproduct N₂O on the Ag surface which is depleted by subsequent photoirradiation. A similar PID signal of N₂ from NO adsorbed on Ag(111) at 85 K has been reported before;² however, it was ascribed to the fragmentation of photodesorbed N₂O and NO in the QMS. By contrast, the intensity of N₂ signal in Figure 1 is about one-half that of N₂O, which is significantly larger than the cracking pattern of the QMS, and does not exhibit the initial plateau seen in the N₂O 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/cm². One immediately notices that the TOF peak in the N₂ data (Trace A) appears much earlier and is narrower than those of the other species. In contrast, the peak in the TOF spectrum of N₂ photodesorbed from a monolayer of N₂O 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 N₂ (the peak in Trace A) is ~5700 K, whereas those of N₂ (Trace B), O₂, N₂O, and NO are 1200, 810, 1200, and 770 K, respectively. We stress that the shapes of TOF spectra of N₂ measured at 2.3 and 3.5 eV

[†] Fritz-Haber-Institut der Max-Planck-Gesellschaft.

[‡] Technische Universität München.

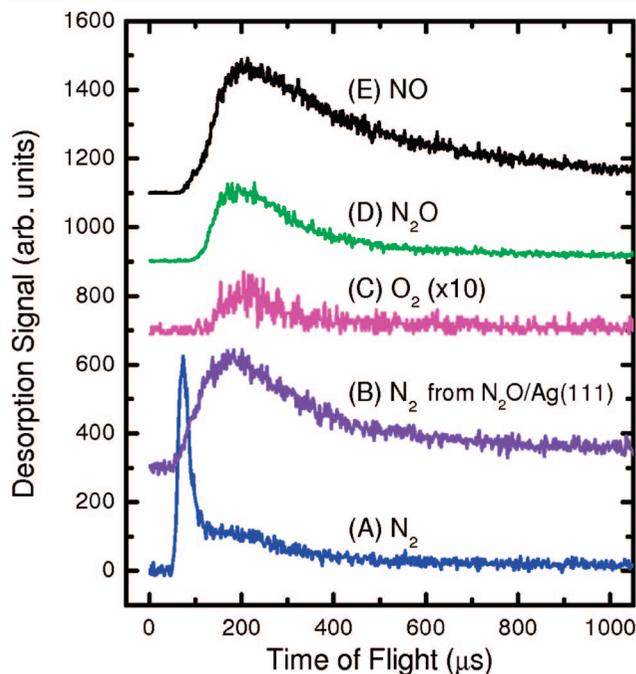


Figure 2. Time-of-flight (TOF) spectra of photoproducts desorbed by 4.7-eV laser irradiation of $(\text{NO})_2/\text{Ag}(111)$ (Traces A, C–E) and $\text{N}_2\text{O}/\text{Ag}(111)$ (Trace B).

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 $(\text{NO})_2$ even at these lower photon energies.

It has been established by previous studies that the photoreactions of $(\text{NO})_2$ on $\text{Ag}(111)$ 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 $(\text{NO})_2$ responsible for photoreaction is located at ~ 2 eV above the Fermi level.⁸ However, the direct photochemical formation of N_2 from $(\text{NO})_2$ has not been identified before, neither on solid surfaces² nor in the gas phase.¹

For the mechanism of the N_2 formation from $(\text{NO})_2$ 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 $(\text{NO})_2$ onto $\text{Ag}(111)$ its N–N bond is contracted from 2.26 \AA to $\sim 1.63\text{ \AA}$, whereas the N–O bond is stretched from 1.15 \AA to $\sim 1.21\text{ \AA}$. Thus, the N–N bond formation becomes feasible for the adsorbed $(\text{NO})_2$.

Once N_2 is formed from an adsorbed $(\text{NO})_2$, 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 $(\text{NO})_2$ on $\text{Ag}(111)$ is $2.11\text{--}2.27\text{ \AA}$,⁸ whereas the equilibrium distance between N_2 and $\text{Ag}(111)$ is 3.68 \AA .¹¹ The resulting strong repulsion causes the extremely high translational temperature ($\sim 5700\text{ K}$) 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, $\text{O}^* + \text{O}^* \rightarrow \text{O}_2$ and/or $\text{O}^* + \text{O}(\text{a}) \rightarrow \text{O}_2$, and not from a first-order process of the NO dimers, $(\text{NO})_2 \rightarrow \text{N}_2 + \text{O}_2$. 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 $(\text{NO})_2$ 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 $(\text{NO})_2$ adsorbed on cold $\text{Ag}(111)$, 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 $(\text{NO})_2$. The Ag surface reduces the N–N bond length of $(\text{NO})_2$ 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.; Stollow, A. *Science* **2006**, *311*, 219. (b) Levchenko, S. V.; Reisler, H.; Krylov, A. I.; Gessner, O.; Stollow, 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) Hertzler, 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