

## RESONANT PHOTOEMISSION OF N<sub>2</sub>O ON Ir(110)

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The adsorption of N<sub>2</sub>O on Ir(110) was investigated with high-resolution resonant photoemission at 135 K. The results obtained show evidence of molecular adsorption of N<sub>2</sub>O, along with some dissociation. It is found that the nitrogen photoemission spectra measured at the terminal and central nitrogen energy positions of the N<sub>2</sub>O/Ir(110) system are equivalent to those of N<sub>2</sub>O in the gas phase. In contrast, the oxygen spectrum shows little resemblance to the gas phase oxygen spectrum of N<sub>2</sub>O. In the nitrogen resonant photoemission spectra one can only discover resonant behavior with constant binding energy peaks. In contrast, the oxygen resonant photoemission spectra shows dominantly Auger behavior with peaks at constant kinetic energies. Both observations reveal that the oxygen is bonded to the Ir surface. A systematic study as a function of coverage and temperature and a comparison with other surfaces differing in structure and composition are needed to understand the variations in the adsorption behavior of N<sub>2</sub>O on metal surfaces.

*Keywords:* X-ray absorption spectroscopy; x-ray photoelectron spectroscopy; nitrogen oxides; nitrogen molecule; adsorption; thermal desorption; iridium; stepped single crystal surfaces.

### 1. Introduction

N<sub>2</sub>O is an important greenhouse gas and it participates in cyclic reactions that lead to ozone destruction.<sup>1–7</sup> In addition, N<sub>2</sub>O is used as an oxidant for the selective oxidation of hydrocarbons, for example benzene to phenol, using iron complexes in the zeolite ZSM5 (Fe-ZSM5) as a catalyst.<sup>8</sup> N<sub>2</sub>O is a linear asymmetric molecule that can be described as a resonance structure between N≡N<sup>+</sup>–O<sup>–</sup> and <sup>–</sup>N=N<sup>+</sup>=O. Its adsorption on metal surfaces is an intriguing subject and a large variety of surface

structures have been reported. Depending on the metal, the coverage, the surface structure and the temperature, either molecular or dissociative adsorption occurs. Molecular adsorption is typical of fcc(111) surfaces of Ir, Ag, Ni, Pt and Pd at temperatures between 50 to 100 K.<sup>9</sup> Dissociative adsorption to Oads and N<sub>2</sub> gas occurs on a series of surfaces, including the (110) surfaces of Ni, Pd, Rh, Ir and Cu. A very interesting observation is that all three constituent atoms, the terminal nitrogen, the central nitrogen and the oxygen, have been reported to bind to the metal surface.<sup>9</sup>

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In order to further enhance our understanding of the  $\text{N}_2\text{O}$ -metal interaction, we studied the adsorption and reactions of this gas on various noble metal surfaces. Previous papers dealt with the  $\text{N}_2\text{O}$  adsorption and reaction with  $\text{H}_2$ <sup>5</sup> and  $\text{CO}$ <sup>6</sup> on the Ir(110) surface. UHV techniques such as MS, LEED and AES were used. The limitation of these studies encouraged us to extend this research to high-resolution resonant photoemission spectroscopy, in an attempt to further investigate the bond nature of the  $\text{N}_2\text{O}$  molecule to the Ir(110) surface. The present letter reports on the first results in this direction.

The resonant photoemission data were recorded at the beam line I511 of MAX-II, at the Swedish National Synchrotron facility MAX-lab. I511 is a new undulator-based beamline for studies in the VUV and soft x-ray region. The end station has two separate chambers for measurements and sample preparation. A Scienta hemispherical electron energy analyzer was used to record the photoelectron spectra. All spectra were obtained at grazing emission and grazing polarization and all binding energy values were relative to the Fermi level. The Ir(110) crystal was cleaned by repetitive cycles of heating in an oxygen or hydrogen atmosphere,  $\text{Ar}^+$  ion sputtering ( $p(\text{Ar}) = 1 \times 10^{-5}$  mbar, incident energy = 1.5 kV) and flashing in UHV to 1200 K. Surface cleanliness was checked with photoemission.

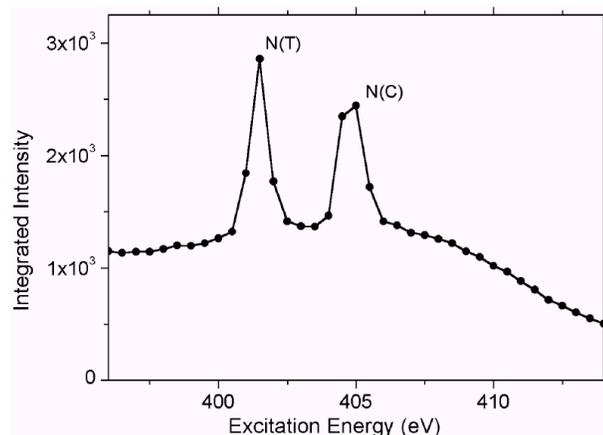


Fig. 1. The nitrogen 1s *x*-ray absorption obtained from integrated signal of resonant photoemission at 135 K on Ir(110) (dots indicate data points where resonant photoemission spectra were taken).

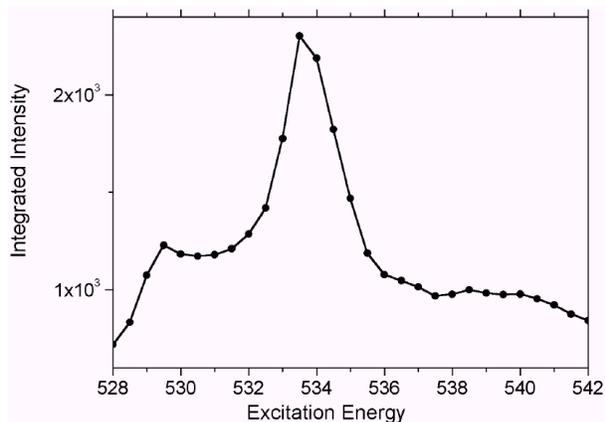


Fig. 2. The oxygen 1s *x*-ray absorption obtained from integrated signal of resonant photoemission at 135 K on Ir(110) (dots indicate data points where resonant photoemission spectra were taken).

Figures 1 and 2 show the nitrogen 1s and oxygen 1s *x*-ray absorption spectra, respectively, obtained from integrated signal of the resonant photoemission spectra at 135 K. These figures are given to indicate the positions at which the resonant photoemission spectra have been measured. For the N1s spectrum (Fig. 1) two peaks are observed, related to the  $\pi^*$  LUMO of respectively the terminal (401 eV) and central (405 eV) nitrogen, following the assignment of Ceballos *et al.*<sup>10</sup> For the O 1s spectrum (Fig. 2), two peaks are also observed. The first small peak (at 529 eV), can be ascribed to adsorbed atomic oxygen  $\text{O}_{\text{ads}}$  and the second peak (at 533 eV) is related to the  $\pi^*$  LUMO of oxygen of  $\text{N}_2\text{O}$ , in agreement with Ref. 10.

These assignments imply that part of the  $\text{N}_2\text{O}$  adsorbs molecularly, while another part adsorbs dissociatively, where the  $\text{N}_2$  desorbs while oxygen remains adsorbed on the surface.<sup>5,6,11</sup> In a previous *x*-ray photoemission (XPS) study dealing with NO adsorption on Ir(110), a peak of atomic O was also found at 529 eV, along with the peak of molecular NO at 531 eV.<sup>3</sup> The existence of molecular adsorption is confirmed by thermal desorption experiments performed at 135 K in the UHV system in Leiden. (Experimental details of this system are described elsewhere.)<sup>5</sup> These results show a single desorption peak around 150 K.

Fast *x*-ray photoelectron (XPS) results showed two peaks of N 1s at 135 K after exposure to  $\text{N}_2\text{O}$ .

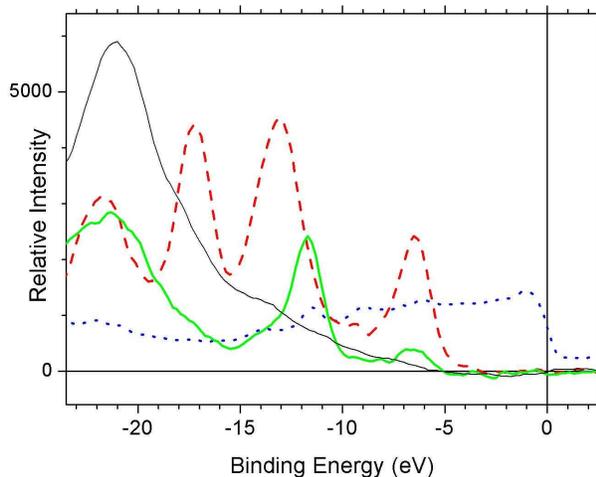


Fig. 3. The resonant photoemission spectra before the nitrogen edge (396 eV: dotted), at the terminal nitrogen (401 eV: dashed), the central nitrogen peak (404 eV: solid) and the oxygen peak (533.5 eV: thin solid).

Its binding energies were around 405 eV and 409 eV. It was observed that after exposure to  $N_2O$  at 135 K, heating the sample 10 K higher resulted in the disappearance of both N 1s peaks, indicating that no more nitrogen was present on the surface. At temperatures higher than 135 K, no N 1s peaks could be observed. This suggests that the N 1s peaks detected are related to molecular adsorption of  $N_2O$ , since this kind of adsorption is generally observed at low temperatures.<sup>11–14</sup> In case of dissociation, the  $N_2$  formed is more likely to be released, as shown above, thus being undetected.

Figure 3 shows the resonant photoemission spectra before the nitrogen edge (396 eV: dotted), at the terminal nitrogen (401 eV: dashed), the central nitrogen peak (404 eV: solid) and the oxygen peak (533.5 eV: thin solid). The three resonant spectra are shown after subtraction of the 396 eV spectrum. This subtracts the Ir-metal intensity, as well as the (very small) direct photoemission of  $N_2O$  (see below). The zero energy is determined from the edge of the off-resonance spectrum and relates to the Fermi energy of  $Ir(110)$ . The terminal nitrogen spectrum shows clearly separated peaks at respectively 6.4 eV, 13.0 eV, 7.3 eV and 21.7 eV. The energy separation as well as intensity variations of this spectrum are essentially a copy of the gas-phase terminal nitrogen spectrum of  $N_2O$ ,<sup>15</sup> with the difference that the binding energies of adsorbed  $N_2O$  are

shifted over  $\sim 6$  eV with respect to the gas-phase binding energies. This is partly due to a different definition of the binding energy, i.e. energy below the Fermi energy for adsorbates respectively difference between x-ray energy and electron energy for gases. The central nitrogen spectrum shows peaks at 6.4 eV, 11.7 eV and 21.3 eV, respectively, again in complete agreement with the gas-phase central nitrogen spectrum of  $N_2O$ .<sup>15</sup> In contrast, the oxygen spectrum is not in agreement with the oxygen spectrum of the gas-phase. Essentially, a single big peak is visible at 21.0 eV. Below, we will argue that this peak relates essentially to an Auger channel and not to a photoemission resonance.

The nitrogen peaks do not shift with excitation energy on the binding energy scale, which indicates that these peaks are related to a direct resonant phenomenon in which the 1s core electron is excited to  $\pi^*$  LUMO of respectively the central and terminal nitrogen and in the resonating Auger decay step the  $\pi^*$  LUMO electron fills the 1s core hole again, during which process a valence electron is excited, a process known as participator Auger. Using a configurational notation this process can be given as  $G > 1s^{-1}\pi^* > V^{-1}$ , where  $G$  is the ground state and  $V^{-1}$  a hole in the valence band. Another resonant decay process could be a channel for which the  $\pi^*$  LUMO electron would not take part in the Auger decay. This process can be indicated as  $GS > 1s^{-1}\pi^* > V^{-2}\pi^*$ , i.e., the  $\pi^*$  electron remains present and one ends up with a valence hole plus an electron-hole excitation. The creation of electron-hole pairs costs energy and one would expect the electrons from such so-called spectator lines at higher (apparent) binding energies. The calculations of Fink<sup>15</sup> include both the participator and spectator Auger channels, and the good correspondence of these calculations with both the gas-phase  $N_2O$  as well as the adsorbed  $N_2O$  implies that one essentially observes both channels. Miron and co-workers compare the resonant Auger spectra with the direct photoemission spectrum of gas phase  $N_2O$ .<sup>16</sup> Direct photoemission gives peaks at binding energies of 13.0, 16.5 and 20.0 eV. Assuming that one would observe the same direct photoemission spectrum for adsorbed species (which is not likely for the oxygen contribution as discussed below), this implies that we expect these peaks at 7.0, 10.5 and 14.0 eV in Fig. 1. Small peaks are indeed observed at 6.0, 9.0, 11.5 and 14.0 eV, respectively. These peaks are

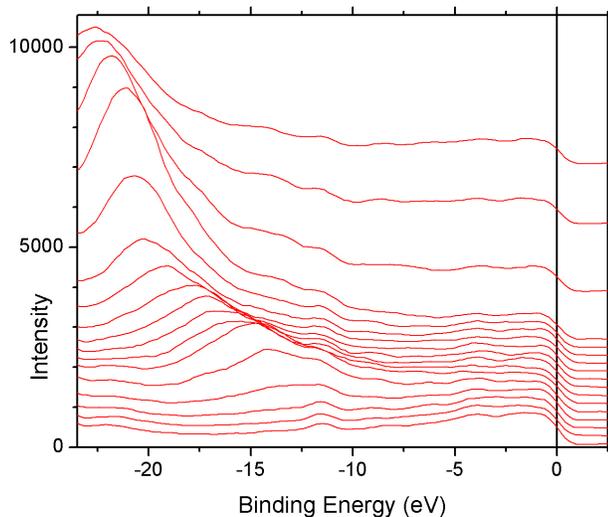


Fig. 4. The oxygen resonant photoemission spectra excited between 527 eV (bottom) and 535 eV (top) in steps of 0.5 eV.

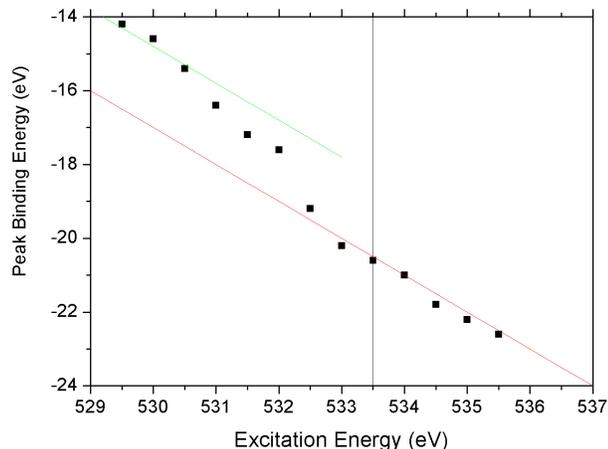


Fig. 5. The binding energies of the oxygen resonant photoemission spectra. The horizontal axis gives the excitation energy. The peak position of the O 1s edge of N<sub>2</sub>O is at 533.5 eV. The vertical axis gives the binding energy with respect to the Fermi level of Ir.

possibly due to the (modified) direct photoemission spectrum, but as they are also affected by the Ir(110) background we cannot draw any detailed conclusion.

Figure 4 shows oxygen resonant photoemission spectra. The spectra are shown at excitation energies ranging from 527 eV (bottom) to 535 eV (top) in steps of 0.5 eV. One observes a spectral shape that contains only a single visible peak that seems to shift

with excitation energy. Figure 5 plots the binding energy peak positions of the oxygen resonant photoemission spectra. One observes that from 532.5 eV, the peak position follows a diagonal line, i.e. a line with constant kinetic energy. Below 531 eV another diagonal line is followed, shifted over 2.2 eV. A diagonal feature in the resonant photoemission plane indicates a normal Auger line. A normal Auger line relates to a process in which the  $\pi^*$  electron delocalizes from the x-ray absorption site and in a following step a valence electron fills the 1s core hole, while a second valence electron is excited. One can write this process as  $GS > 1s^{-1}\pi^* \gg 1s^{-1} > V^{-2}$  and the final state is given by the energy difference between  $1s^{-1}$  and  $V^{-2}$ . This effectively implies that the excited electron is transferred to the substrate faster than the core hole decays.

Normal Auger decay processes are expected to dominate over resonant Auger processes if an excited electron from a core level to  $\pi^*$  has delocalization character caused by the  $\pi^*$ -d hybridization.<sup>2,4</sup> The oxygen edge of N<sub>2</sub>O is clearly dominated by a normal Auger, similar to, for example, the N edge of NO on Rh.<sup>4</sup> The nitrogen edges of N<sub>2</sub>O behave completely different and are dominated by resonant Auger processes. Hence, the oxygen  $\pi^*$  electron delocalizes while the nitrogen  $\pi^*$  electrons do not delocalize, leading to the conclusion that the oxygen of N<sub>2</sub>O is strongly bonded to the Ir(110) surface and the nitrogen atoms are not (strongly) bonded, which is also evident from the fact that the nitrogen spectra are essentially identical to the gas phase N<sub>2</sub>O spectra. Therefore, one can conclude that the N<sub>2</sub>O molecule binds to the Ir(110) surface via the oxygen atom.

In conclusion, we can say that the resonant photoemission experiments at the oxygen and nitrogen edges reveal very interesting information regarding the electronic structure of the N<sub>2</sub>O/Ir(110) system. The analysis of the spectra shows that the oxygen is bonded to the Ir surface and that a range of valence (and  $V^{-2}\pi^*$ ) states are found for the nitrogen atoms, in close analogy to the respective gas-phase spectra. It is perhaps surprising that the central and terminal nitrogen in N<sub>2</sub>O have such different spectral shapes and that they have essentially the same shape in the gas phase and in adsorbates that are bound via oxygen to the surface. Both observations imply that the resonant Auger spectra in molecules

as well as adsorbates are highly local processes that are only little affected by changes further away than their nearest neighbor.

To further elucidate the adsorbed N<sub>2</sub>O systems, we plan to study the N<sub>2</sub>O/Ir(110) system as a function of temperature and coverage. In addition, a comparison with other surfaces and metals would allow crucial insight into the questions concerning the variations in the adsorption behavior of N<sub>2</sub>O in these systems. Also, one can perform similar experiments on polycrystalline surfaces and oxide surfaces, in order to study systems that are more relevant for actual catalytic reactions involving N<sub>2</sub>O. Recent developments in *in situ* photoemission experiments would allow such experiments at pressures up to a few mbar.<sup>17,18</sup>

## References

1. D. E. Ibbotson, T. S. Wittrig and W. H. Weinberg, *Surf. Sci.* **110** (1981) p. 313.
2. A. Sandell, O. Björneholm, A. Nilsson, B. Hernnäs, J. N. Andersen and N. Mtensson, *Phys. Rev. B* **49** (1994) p. 10136.
3. C. A. de Wolf, J. W. Bakker, P. T. Wouda, B. E. Nieuwenhuys, A. Baraldi, S. Lizzit and M. Kiskinova, *J. Chem. Phys.* **113** (2000) p. 10717.
4. T. Saito, M. Imamura, N. Matsubayashi, F. Furuya, T. Kikuchi and H. Shimada, *J. Electron Spectrosc. Relat. Phenom.* **119** (2001) p. 95.
5. S. A. Carabineiro and B. E. Nieuwenhuys, *Surf. Sci.* **495** (2001) p. 1.
6. S. A. C. Carabineiro, W. D. van Noort and B. E. Nieuwenhuys, *Catal. Lett.* **84** (2002) p. 135.
7. S. A. C. Carabineiro, W. D. van Noort and B. E. Nieuwenhuys, *Surf. Sci.* 532–535 (2003) p. 96.
8. W. M. Heijboer, A. A. Battiston, A. Knop-Gericke, M. Hävecker, H. Bluhm, B. M. Weckhuysen, D. C. Koningsberger and F. M. F. de Groot, *Phys. Chem. Chem. Phys.* **5** (2003) p. 4484.
9. A. V. Zeigarnik, *Kinet. Catal.* **44** (2003) p. 233.
10. C. Ceballos, H. Wende, K. Baberschke and D. Arvantis, *Surf. Sci.* **482** (2001) p. 15.
11. Y. Ohno, I. Kobal, H. Horino, I. Rzeznicka and T. Matsushima, *Appl. Surf. Sci.* 169–170 (2001) p. 273.
12. K. Sawabe and T. Matsumoto, *Chem. Phys. Lett.* **194** (1992) p. 45.
13. Y. Matsumoto, J. Lee, H. Kato and K. Sawabe, *Proc. SPIE 2125, Laser Techniques for Surface Science*, eds. H.-L. Dai and S. J. Sibener (1994) p. 303.
14. S. Haq and A. Hodgson, *Surf. Sci.* **463** (2000) p. 1.
15. R. Fink, *J. Elec. Spec.* **76** (1995) p. 295.
16. C. Miron, M. Simon, P. Morin, S. Nanbu, N. Kosugi, S. L. Sorensen, A. N. de Brito, M. N. Piancastelli, O. Bjorneholm, R. Feifel, M. Bassler and S. Svensson, *J. Chem. Phys.* **115** (2001) p. 864.
17. A. Knop-Gericke, M. Hävecker, T. Schedel-Niedrig and R. Schlögl, *Top. Catal.* **10** (2000) pp. 187.
18. W. M. Heijboer, A. A. Battiston, A. Knop-Gericke, M. Hävecker, R. Mayer, H. Bluhm, R. Schlögl, B. M. Weckhuysen, D. C. Koningsberger and F. M. F. de Groot, *J. Phys. Chem. B* **107** (2003) p. 13069.