



HAL
open science

A Combination of DFT and Spectroscopy Solves Photocatalytic Mechanisms: the Case of N-O bonds

Emmanuel Nicolas, Marianne Kjellberg, Zineb El Moqaouil, Lucile Anthore-Dalion, Annamaria Quaranta, Thibault Cantat

► To cite this version:

Emmanuel Nicolas, Marianne Kjellberg, Zineb El Moqaouil, Lucile Anthore-Dalion, Annamaria Quaranta, et al.. A Combination of DFT and Spectroscopy Solves Photocatalytic Mechanisms: the Case of N-O bonds. DFT 2024, Aug 2024, Paris, France. hal-04689021

HAL Id: hal-04689021

<https://hal.science/hal-04689021v1>

Submitted on 5 Sep 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial - NoDerivatives 4.0 International License

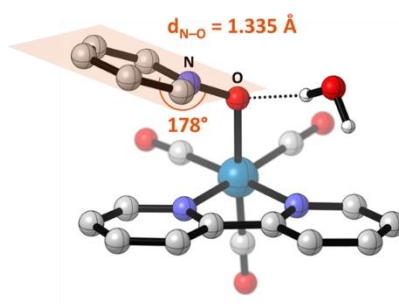
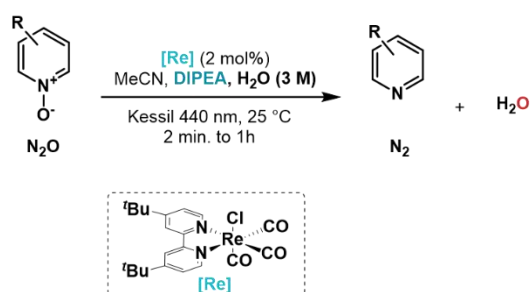
A Combination of DFT and Spectroscopy Solves Photocatalytic Mechanisms: the Case of N–O bonds

MARIANNE KJELLBERG,¹ ZINEB EL MOQAOUIL,^{1,2} LUCILE ANTHORE-DALION,¹
ANNAMARIA QUARANTA,² THIBAUT CANTAT¹ AND EMMANUEL NICOLAS¹

1. NIMBE, CEA, CNRS, Université Paris-Saclay, CEA Saclay, 91191 Gif-sur-Yvette Cedex, France
2. Université Paris-Saclay, CEA, CNRS, Institute for Integrative Biology of the Cell (I2BC), 91198 Gif-sur-Yvette, France

emmanuel.nicolas@cea.fr

The accumulation of nitrogen oxides in the environment calls for new pathways to interconvert the various oxidation states of nitrogen, and especially their reduction. However, the large spectrum of reduction potentials covered by nitrogen oxides makes it difficult to find general systems capable of efficiently reducing various *N*-oxides. Nitrous oxide N_2O is a thermodynamic oxidant but has a very low reactivity; on the contrary, pyridine *N*-oxide is an organic substrate with a more challenging reduction potential. We developed in the group a new pathway that enables to reduce both N_2O back to nitrogen and pyridine *N*-oxide to pyridine at room temperature by means of photocatalysis using $[Re(bpy)(CO)_3Cl]$, traditionally used to deoxygenate CO_2 . Herein, the mechanism of the N–O bond deoxygenation will be described for both substrates. It used a combination of multiple techniques, including laser flash photolysis, spectroelectrochemistry, NMR and infrared spectroscopy, together with computational studies (DFT).



References

- [1] M. Kjellberg, A. Ohleier, P. Thuéry, E. Nicolas, L. Anthore-Dalion, T. Cantat, *Chem. Sci.* **2021**, *12*, 10266-10272.