



# Structural dynamics of nitrosylruthenium isomeric complexes studied with steady-state and transient pump-probe infrared spectroscopies



Yan Zhao<sup>a,b,c,1</sup>, Fan Yang<sup>b,c,1</sup>, Jianru Wang<sup>d</sup>, Pengyun Yu<sup>b,c</sup>, Huifen Pan<sup>e</sup>, Hongfei Wang<sup>e,\*</sup>, Jianping Wang<sup>b,c,\*\*</sup>

<sup>a</sup> College of Physics & Electronics Engineering, Shanxi University, Taiyuan 030006, China

<sup>b</sup> Molecular Reaction Dynamics Laboratory, Beijing National Laboratory for Molecular Sciences, Beijing 100190, China

<sup>c</sup> Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

<sup>d</sup> Institute of Opto-Electronics, Shanxi University, Taiyuan 030006, China

<sup>e</sup> Key Laboratory of Energy Conversion and Storage Materials of Shanxi Province, Institute of Molecular Science, Shanxi University, Taiyuan 030006, China

## ARTICLE INFO

### Article history:

Received 15 January 2016

Received in revised form 25 April 2016

Accepted 27 April 2016

Available online 7 May 2016

### Keywords:

Nitrosyl

Ruthenium complex

Isomer

Structural dynamics

Femtosecond IR pump-probe spectroscopy

## ABSTRACT

The characteristic nitrosyl stretching (NO) in the region of 1800–1900 cm<sup>-1</sup> was used to study the geometric and ligand effect on two nitrosylruthenium complexes, namely [Ru(OAc)(2QN)<sub>2</sub>NO] (QN = 2-chloro-8-quinolinol (H2cqn) or QN = 2-methyl-8-quinolinol (H2mqn)). The NO stretching frequency ( $\nu_{\text{NO}}$ ) was found in the following order:  $\nu_{\text{cis-1}}(2\text{cqn}) > \nu_{\text{cis-2}}(2\text{cqn}) > \nu_{\text{cis-1}}(2\text{mqn}) > \nu_{\text{trans}}(2\text{mqn})$ . The results exhibited a spectral sensitivity of the NO mode to both charge distribution and ligand arrangement, which was supported by ab initio computations and natural bond orbital (NBO) analyses. Further, the vibrational population of the vibrationally excited NO stretching mode was found to relax on the order of 7–10 ps, showing less than 30% variation from one isomer to another, which were explained on the basis of NO local structures and solute-solvent interactions in these isomeric nitrosylruthenium complexes.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Nitric oxide (NO) is a highly reactive messenger molecule that plays an important role in regulating the immune, nervous, and cardiovascular systems of mammals. Coordination of NO with metal ion effected on the generation, translocation, and action of nitric oxide in living systems. A well known example is sodium nitroprusside (SNP, Na<sub>2</sub>[Fe(NO)(CN)<sub>5</sub>]), which has been used in clinical therapy as a powerful NO-donor and was an ideal model for probing Fe–NO bonding in several heme–NO proteins [1,2]. However, these iron-based nitrosyl complex release NO spontaneously, and produced CN ligand is obviously toxic with side effects. As a result, considerable attention were paid on the nitrosylruthenium complex, which with favorable activity and stability in biological conditions [3–6].

Understanding the characteristic structures and dynamics of metal–NO complexes, or metal nitrosyls, is critical to the understanding of the important role played by nitric oxide in biological signaling processes [7–10]. The fashion of the NO group coordination to a transitional

metal center can significantly regulate the electronic structure and the reactivity of a given NO-complex [11–14]. The NO group has a unique stretching vibration ( $\nu_{\text{NO}}$ ) whose frequency and band profile are sensitive to the conformation and chemical environment of the nitrosyl metal complexes.

Linear infrared spectroscopy (in particular the conventional FTIR spectroscopy) offers an excellent opportunity for characterizing the structural, vibrational, and reactivity properties of the NO-contained molecular species, because the NO group itself can serve as a characteristic spectroscopic probe for such purpose [15–20]. For the nitrosylruthenium complexes, the peculiarity of [Ru(II)–NO<sup>+</sup>] group affects their structure and reactivity. The {Ru–NO}<sup>6</sup> configuration is generally believed to be NO<sup>+</sup> bound to a Ru(II) center, largely based on the NO stretching mode that is shifted and falls into the frequency region of 1800–1950 cm<sup>-1</sup>. Such a stretching vibration is conveniently located in a less crowded infrared spectral region. Furthermore, binding to metal center can increase the vibrational transition dipole moment of the NO stretching vibration, which results in an enhanced absorption peak.

On the other hand, time-resolved nonlinear infrared spectroscopy, as a dynamical tool, can be used to unravel the structural dynamics of condensed-phase molecules on a wide range of time scales [21–27]. In our recent work, ultrafast two-dimensional infrared (2D IR) spectroscopy has been used to characterized spectral diffusion time, a key parameter for

\* Corresponding author.

\*\* Correspondence to: J. Wang, Molecular Reaction Dynamics Laboratory, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China.

E-mail addresses: [wanghf@sxu.edu.cn](mailto:wanghf@sxu.edu.cn) (H. Wang), [jwang@iccas.ac.cn](mailto:jwang@iccas.ac.cn) (J. Wang).

<sup>1</sup> Authors contributing equally to this work.

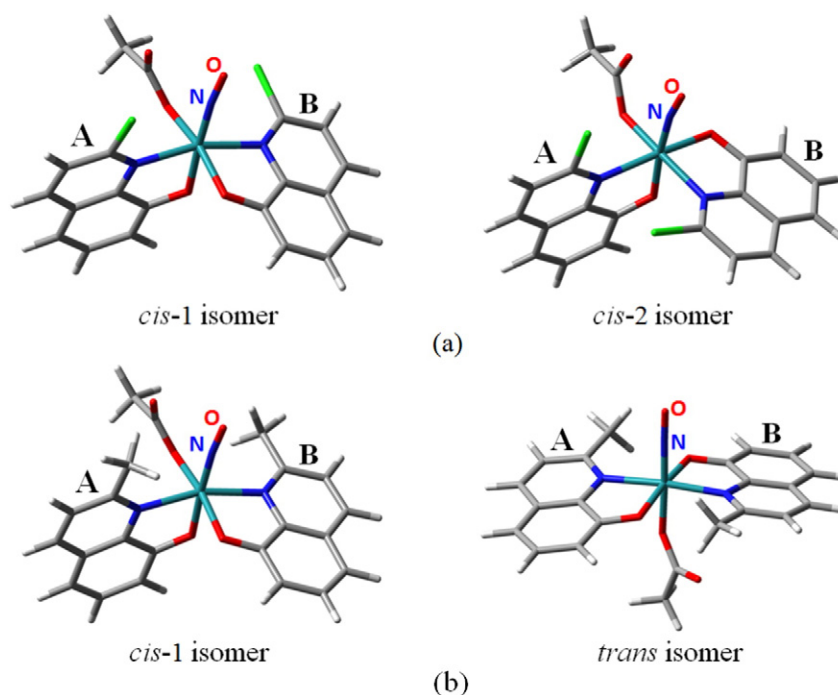


Fig. 1. Structures of the *cis*-1, *cis*-2 [Ru(OAc)(2cqcn)<sub>2</sub>NO] isomers (a) and *cis*-1, *trans* [Ru(OAc)(2mqcn)<sub>2</sub>NO] isomers (b).

equilibrium structural dynamics that is closely associated with the frequency time-correlation function, of the [Ru(OAc)(2cqcn)<sub>2</sub>NO] (H2cqcn = 2-chloro-8-quinolinol) isomers in solution phases [28].

In this work, magic-angle pump-probe infrared spectroscopy, which is also a well-known nonlinear infrared method, was used to investigate the transient spectral and structural behaviors of four nitrosylruthenium (II) complexes, with the aid of linear infrared method and ab initio computations. Specifically, the structural dynamics of *cis*-1 and *cis*-2 [Ru(OAc)(2cqcn)<sub>2</sub>NO] isomers were further studied and compared with those of *cis* and *trans* [Ru(OAc)(2mqcn)<sub>2</sub>NO] (H2mqcn = 2-methyl-8-quinolinol) in CDCl<sub>3</sub>, using the  $\nu_{\text{NO}}$  stretching mode as a structural probe. In the 2-position of 2cqcn, the chlorine atom has an electron attractive nature, while the methyl group has an electron donating nature in the 2-position of coordinated 2mqcn. The structures of the *cis*-1, *cis*-2 and *trans* isomers are shown in Fig. 1. Spectral dynamic characteristics of the geometrical isomers and the effect of different ligands were examined in order to understand the physicochemical reactivity of the nitrosylruthenium (II) complexes.

## 2. Experiments and calculations

### 2.1. Reagents and synthesis

Chemical reagents and solvents were purchased from Sigma and locally available sources. The *cis*-1, *cis*-2 [Ru(OAc)(2cqcn)<sub>2</sub>NO] and *cis*-1 [Ru(OAc)(2mqcn)<sub>2</sub>NO] were synthesized according to the previously described procedure [29–31]. The *trans* [Ru(OAc)(2mqcn)<sub>2</sub>NO] complex was prepared by photoisomerization from *cis*-1 isomer. All the isomeric complexes were confirmed by proton NMR spectra. DMSO-*d*<sub>6</sub> (with 99.9% D/H exchange, Cambridge Isotope Laboratories) was used as a solvent and the chemical shifts were referred to an internal TMS (0.03% V/V). The proton NMR spectra were recorded on a Bruker 600 M spectrometer.

### 2.2. FT-IR experiment

The *cis*-1, *cis*-2 [Ru(OAc)(2cqcn)<sub>2</sub>NO] and *cis*-1, *trans* [Ru(OAc)(2mqcn)<sub>2</sub>NO] isomeric complexes were dissolved in CDCl<sub>3</sub> at

appropriate concentrations. The sample solutions were loaded between two 25-mm diameter and 2-mm thick CaF<sub>2</sub> windows separated by a 50- $\mu\text{m}$  Teflon spacer. FT-IR spectra of the *cis* and *trans* isomers in the mid-IR frequency region were collected using a Nicolet 6700 spectrometer (Thermo Electron) at 1-cm<sup>-1</sup> resolution. All experiments were performed at room temperature (22 °C).

### 2.3. IR pump-probe experiment

Nonlinear IR experiment was performed using a home-built transient IR spectrometer. A commercial ultrafast Ti:sapphire laser amplifier generated a 3-mJ, 35-fs, 800-nm pulse at a repetition rate of 1 kHz. The laser was used to pump an optical parametric amplification (OPA) to generate a signal idler pulse pair in the near IR region, which was used to produce a 70-fs, 5- $\mu\text{J}$  mid-IR pulse by difference frequency generation process using a 0.5-mm thick type-II AgGaS<sub>2</sub> nonlinear crystal. The obtained IR pulse was tuned to have a center frequency of 1850 cm<sup>-1</sup> with a full-width at half-maximum (FWHM) of ca. 250 cm<sup>-1</sup>. The vibrational population relaxation dynamics were examined at the magic-angle

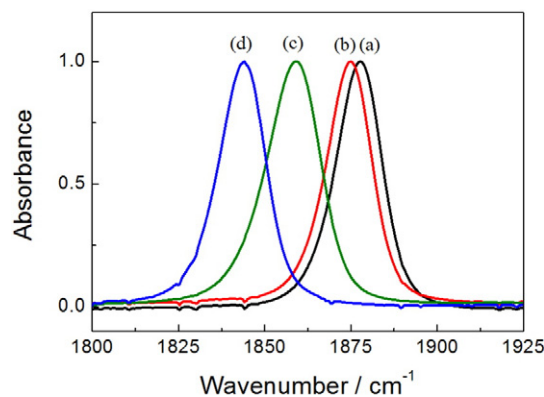


Fig. 2. Normalized linear IR spectra in the NO stretching region of the *cis*-1 (a) and *cis*-2 [Ru(OAc)(2cqcn)<sub>2</sub>NO] (b) isomer, and those of *cis*-1 (c) and *trans* [Ru(OAc)(2mqcn)<sub>2</sub>NO] (d) complexes in CDCl<sub>3</sub>.

Download English Version:

<https://daneshyari.com/en/article/1230648>

Download Persian Version:

<https://daneshyari.com/article/1230648>

[Daneshyari.com](https://daneshyari.com)