

Light Induced Metastable State of Silver Nitroprusside Probed by Raman Spectroscopy

Pallavi Ghalsasi^{1,*}, Prasanna Ghalsasi², A. Thomas³, D.V.S. Muthu³
and A.K. Sood³

¹*School of Engineering and Technology, Navrachana University, Vadodara- 391 410, Gujarat, India*

²*Department of Chemistry, The M.S. University of Baroda, Vadodara- 390 001, Gujarat, India*

³*Department of Physics, Indian Institute of Science, Bangalore-560 012, Karnataka, India*

**E-mail:pallavi.teredesai@gmail.com*

Abstract. Low temperature Raman spectroscopic measurements on silver nitroprusside (AgNP), $\text{Ag}_2[\text{Fe}(\text{CN})_5\text{NO}]$ powders display reversible features of a partially converted metastable state. The results are compared with similarly observed metastable state in case of sodium nitroprusside (NaNP) and the differences have been discussed in terms of possible resistance to metastable state formation offered by silver atoms on the basis of hard soft acid base (HSAB) theory.

Keywords: Nitroprusside, Metastable state, Raman spectroscopy

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INTRODUCTION

Silver nitroprusside (AgNP), $\text{Ag}_2[\text{Fe}(\text{CN})_5\text{NO}]$ is an analogue of sodium nitroprusside (NaNP), $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$. The well known applications of the latter include its use as a Mössbauer calibration standard and as a vasodilator in biomedical sciences. NaNP has also drawn a considerable attention for its potential use as an optical switch information storage material owing to its light induced reversible metastable state below 160K with an extremely long lifetime $\tau > 10^7$ seconds [1]. There are many reports in the literature probing the metastable state of NaNP by optical techniques like Raman scattering [2], infrared spectroscopy [3], optical absorption [4], and time dependent optical transmission [5] to study the population dynamics. A very few reports have also tried to explain the origin of the metastable state [5] and the reason behind its long lifetime [6]. Followed by this discovery in NaNP, it was reported by Zollner et al. [7] using differential scanning calorimetry (DSC), that a series of nitroprussides with different cations and replaced CN and NO ligands also show similar metastable states with irradiation of light. To our knowledge, present work is the first report investigating light induced metastable state in nitroprusside family of complexes other than sodium nitroprusside using Raman spectroscopy.

EXPERIMENTAL

AgNP was synthesized by mixing aqueous solutions of sodium nitroprusside dehydrate, $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$ (298 mg in 10 ml H_2O) and AgNO_3 (340 mg in 10 ml of H_2O). The mixture was stirred at room temperature for about 10 minutes till a peach colour precipitate is formed. The precipitate is then washed with distilled water, filtered and dried at room temperature for one day. The resultant compound was obtained in the form of powder. Samples were characterized by FTIR transmission spectroscopy.

Low temperature micro-Raman spectra were measured on AgNP up to 4K using Oxford Instruments Liquid Helium cooled micro-cryostat and a triple grating DILOR XY Raman Spectrometer. Sample was excited using 514.5 nm line from an Argon ion laser. The measurements have been done in the warming cycle from 4K to 300 K. The laser power had to be maintained extremely low to avoid burning of the sample.

RESULTS AND DISCUSSION

The crystal structure of silver nitroprusside (AgNP) is monoclinic with four molecules per unit cell. The $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ ions form slightly distorted octahedra