

# Back-Bonding Signature with High Pressure: Raman Studies on Silver Nitroprusside

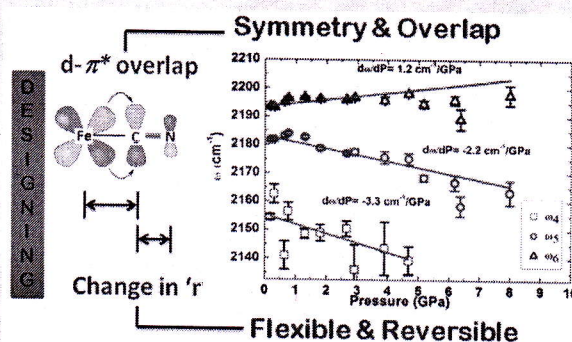
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**ABSTRACT:** In centrosymmetric molecules, like  $A^{n+}[M-(CN)_6]^{n-}$  (where A is alkali metal cation), normally all stretching vibrations of cyanide ( $CN^-$ ) shift to high frequency in response to nonhydrostatic pressure, whereas, in non-centrosymmetric molecules in which one axial  $CN$  ligand is replaced by  $NO$  ligand, one observes unusual softening of only equatorial  $CN$  stretching modes. This effect is pronounced when  $A^+$  is replaced by  $Ag^+$  with difference in coordination ability of latter, resulting in expression of characteristic signature of back-bonding. One can correlate this uneven stretching of cyanide to Poisson-like effect, where the axial  $Fe-N$ ,  $Fe-C$ , and  $C-N$  stretching modes harden but the equatorial  $C-N$  stretching modes soften due to expansion at the equatorial plane. Thus, the present study is focused on results of non-hydrostatic high-pressure Raman measurements on silver nitroprusside up to 11.5 GPa, for not only observing characteristic signature of “back-bonding” interaction, rarely featured in literature, but also for generating reversible flexible structures akin to noncovalent interaction.



## INTRODUCTION

Back-bonding has remained one of the unique “synergistic” *modus operandi* between metal cation and  $\pi$ -acceptor ligand, primarily due to  $\sigma$ -donation and later  $\pi$ -acceptance by ligand.<sup>1</sup> It is the topological arrangement of metal ions’ d-orbitals and  $\pi^*$ -orbitals of ligand that drives such a formation. This not only results in change in bond distance between metal and ligating atoms but is also responsible for unusual conductivity, magnetism, and dynamic properties such as optical behavior,<sup>2–5</sup> light-induced reversible metastable states,<sup>6,7</sup> and structural stability.<sup>8</sup> Most common examples of  $\pi$ -acceptor ligands remain restricted to  $CO$ ,  $CN$ , to some extent  $NO$ , and aromatic amines.

Traditionally, one of the factors that made back-bonding interesting is due to its “characteristic” signature in Fourier transform infrared (FT-IR) or vibrational spectroscopy.<sup>9–11</sup> Unfortunately this technique cannot distinguish between  $\sigma$ -donation and  $\pi$ -back-donation, which remains a challenging assignment. But, now with the combined help from extended X-ray absorption spectroscopy (EXAS) study and theoretical calculations, one can predict percent contribution of various bonding electrons.<sup>12,13</sup>

Back-donation literature leads two important facts: (1) in case of  $CN$  as a ligand,  $\sigma$ -donation results in shortening of  $C-N$  distance, whereas  $\pi$ -backdonation lengthens it (shortens  $Fe-C$  bond). This observation has a periodic trend and therefore has correlation with vibrational frequencies; (2) rarely employed as a tool in designing structures.<sup>4–16</sup> This may be

because  $\pi$ -acceptor ligand during back-bonding prefers *trans*-position or remains in a pair opposite to each other around a metal center. Such a centrosymmetric arrangement of ligand actually removes the “elastic or flexible” nature of back-bonding and may restrict expression of its noncovalent interaction ability in design. We are presently involved in exploring this latter aspect of back-donation and its usefulness in generating technologically important property and/or its characteristic signature.<sup>17–19</sup>

Distance between  $C-N$  bond or  $Fe-C$  bond in  $K_3[Fe(CN)_6]$  or  $K_4[Fe(CN)_6]^{13}$  undergo isotropic change when subjected to temperature or pressure. Change of counterion from  $K^+$  to  $Na^+$  made no difference. One may conclude that centrosymmetric arrangement of ligand around metal center is responsible for isotropic behavior. Interestingly, literature has shown  $CN$  bonds have “isotropic effect” even if the centrosymmetric arrangement of  $-CN^-$  is broken, a case study of  $Na_2[Fe(NO)(CN)_5]$ .<sup>20</sup> Sodium nitroprusside has been studied for its vasodilator application<sup>21</sup> along with related studies focused on understanding physiological role of nitric oxide,  $NO$ .<sup>22,23</sup>

Recently it has been shown that negative thermal expansion ability in hexacyano systems can be observed by replacing  $Na^+$  with  $Ag^+$  due to presence of argentophilic interaction.<sup>24,25</sup> That means  $Ag^+$ , due to its size and coordinating ability, helped in

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