VIBRATIONAL SPECTRA AND STRUCTURES OF METAL (Ti, Ni, Pd) MONONITROSYL COMPLEXES. AN IR MATRIX ISOLATION AND DFT STUDY

LAHOUARI KRIM, M. ESMAIL ALIKHANI and LAURENT MANCERON, *LAPDIR/Spectroschimie Moléculaire, UMR7075 CNRS-P6, Université Pierre et Marie Curie, Bat F74, Boîte 49, 4 place Jussieu, 75252 Paris, Cedex 05, France.*

The infrared spectra of nickel, palladium and titanium mononitrosyl isolated in solid argon at low temperature have been reinvestigated. Two kinds of mechanisms of reactions metal-NO have been observed : In the Ni + NO and Pd + NO experiments, concentration and photochemical studies demonstrate the existence of two isomeric forms of NiNO and only one isomeric form of PdNO with a bent structure. In the NiNO complex case, analyses of the $^{58}Ni/^{60}Ni$, $^{14}N/^{15}N$ and $^{16}O/^{18}O$ isotopic effects indicate that a first form has an end-on bent configuration (as with palladium), and a second form has a cyclic structure, in which the NO ligand is significantly more perturbed. Reversible conversion is achieved by photo selective UV-Visible excitation.

In the Ti + NO experiments, no side-bonded TiNO form has been observed and insertion reaction doesn't need any appreciable activation energy. All three modes of the N-Ti-O insertion product are detected. Comparisons between the Ni+NO, Pd+NO and Ti+NO systems are presented.

Density Functional calculations of the geometrical, electronic and vibrational properties of these isomers are also presented and compared to the experimental values. Isomerization energies have been estimated.