Spectroscopic and Computational Characterization of Lanthanum-Mediated C-H and N-H Bond Activation of Amines

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Abstract

❖ Metal-mediated bond activation of small organic and inorganic molecules plays critical roles in chemical transformation of small molecules into value-added products.

❖ This is because few of such chemical reactions would occur under mild conditions without the metal activation.

❖ In this work, lanthanum atom reactions with alkylamines are carried out in a laser-ablation supersonic molecular beam source; C-H and N-H bond activation in these species is investigated.

❖ The reaction products are observed with photoionization time-of-flight mass spectrometry and characterized by mass-analyzed threshold ionization (MATI) spectroscopy and theoretical calculations.

❖ Adiabatic ionization energy and metal-ligand and ligand-based vibrational frequencies of several short-lived lanthanum complexes are measured from MATI spectra.

❖ Molecular structures, electronic states, and formation mechanisms of these complexes are identified by combining the spectroscopic measurements with density functional theory calculations and spectral simulations.

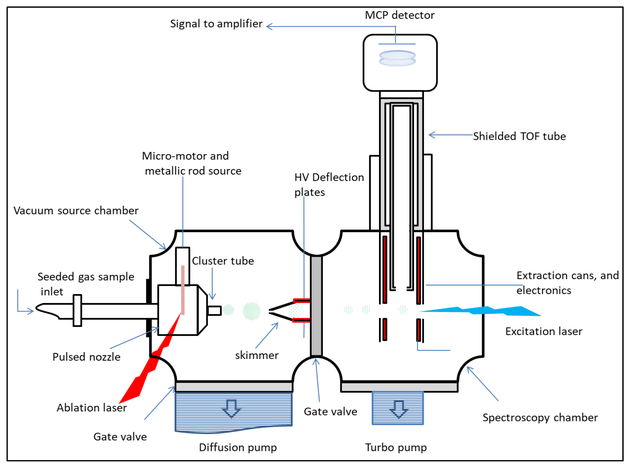
Computational Details

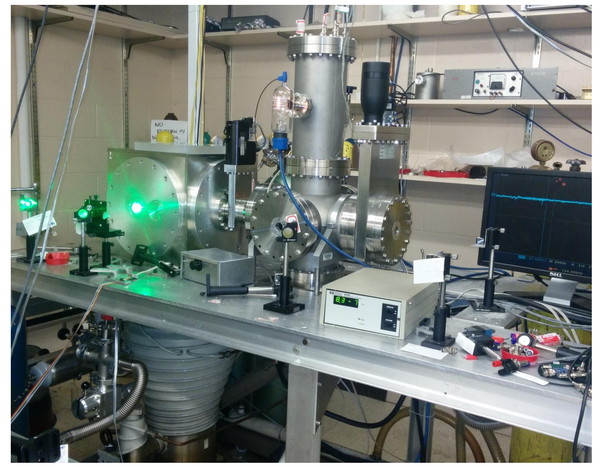
❖ Molecular structure optimization, binding energies, intrinsic reaction coordinates (IRC), adiabatic ionization energies (AIE) are calculated using density functional theory (DFT) at B3LYP level of theory

❖ Single point energy calculations: CCSD(T) with ZPE correction from B3LYP calculations

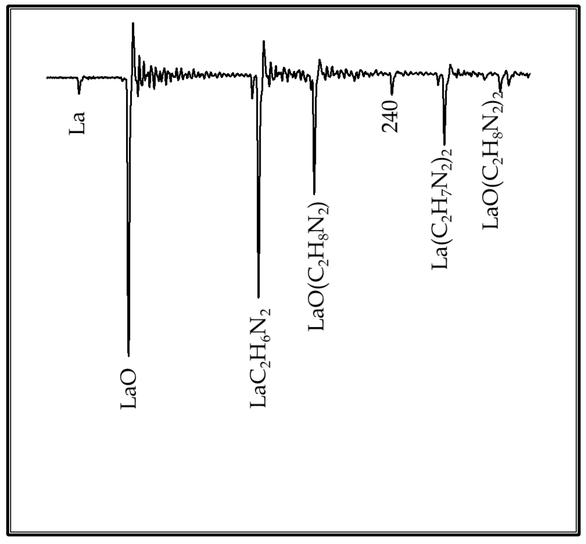
❖ Basis sets used: aug-cc-pVTZ , 6-311+G(d,p) for Carbon, Hydrogen, and Nitrogen; effective-core potential SDD basis set for Lanthanum

MATI Spectroscopy - Experimental Setup

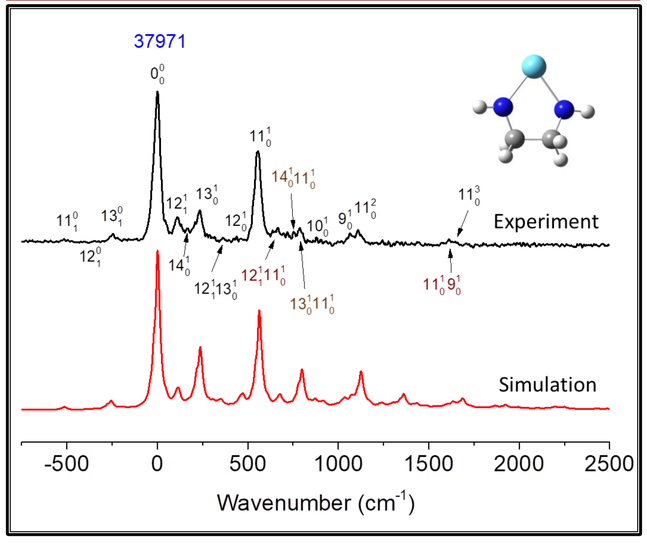




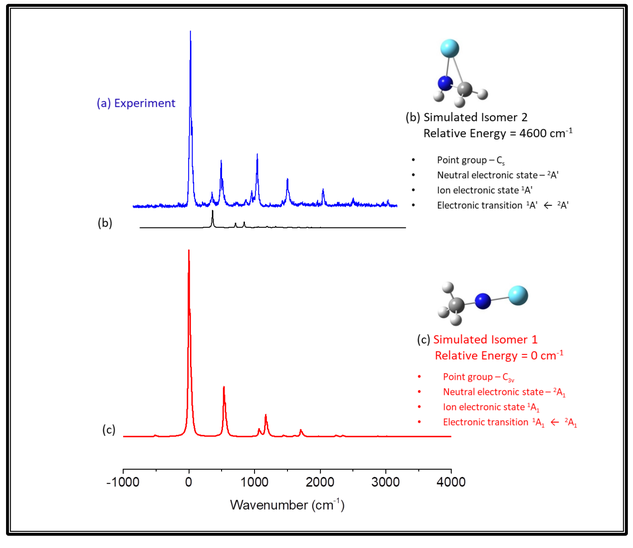
TOF Mass Spectrum of the La + Ethylenediamine Reaction



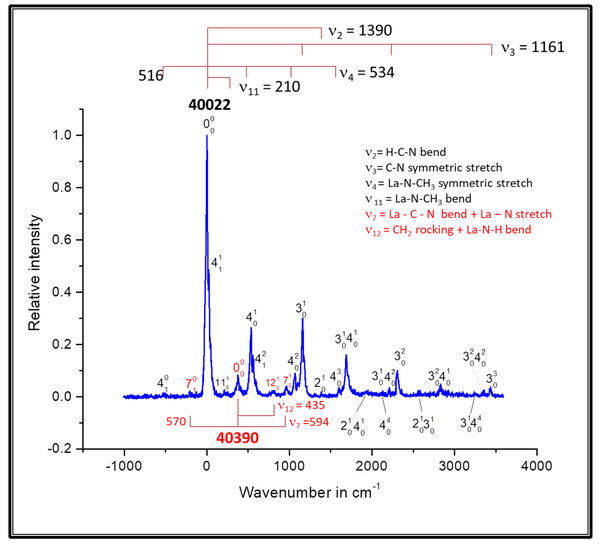
MATI Spectrum of $LaC_2H_6N_2$



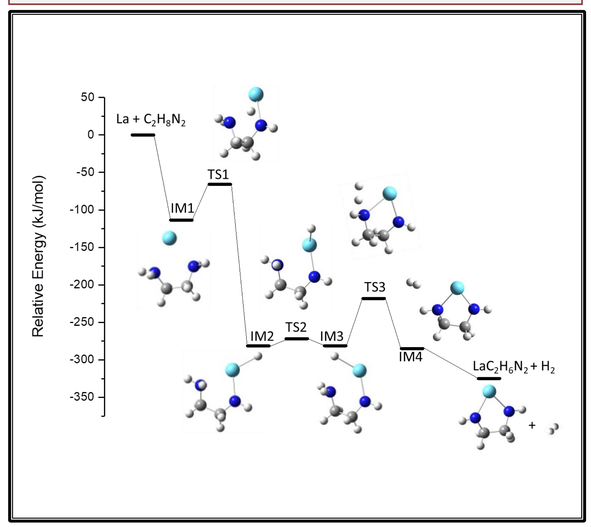
Comparison of Experimental and Simulated Spectra of $La(NCH_3)$ Isomers



MATI Spectrum of $La(NCH_3)$



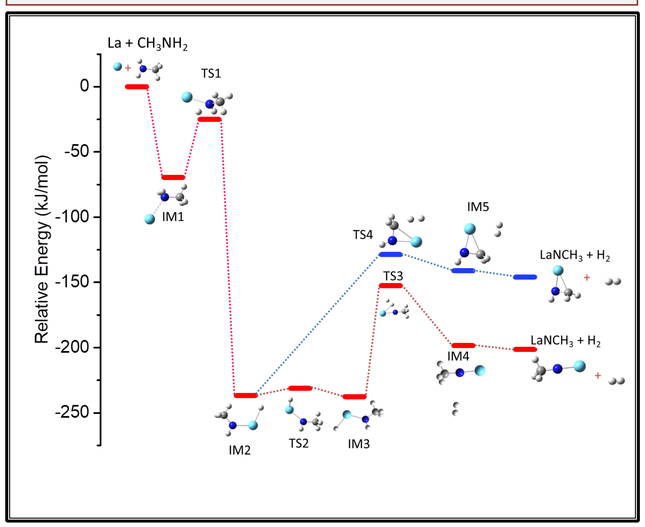
Reaction Pathway for the Formation of $LaC_2H_6N_2$



AIE and Vibrational Frequencies for $LaC_2H_6N_2$ from La + Ethylenediamine Reaction

$LaC_2H_6N_2$: Symmetry-C_2	MATI	B3LYP 6-311+G(d,p)	Mode description
AIE[$^1A \leftarrow {}^2A$]	37971	38486	
ν^+_{14}	165	168	La-Ligand bend
ν^+_{13}/ν_{13}	233/247	237/256	La-Ligand bend, CH_2 rock
ν^+_{12}/ν_{12}	442/346	466/353	La-N asymmetric stretch
$\nu^+_{12} - \nu_{12}$	112	114	
ν^+_{11}/ν_{11}	557/511	562/517	La-N symmetric stretch
ν^+_{10}	881	871	C - C and C – N symmetric stretch
ν^+_{9}	1065	1069	C – C and C-N asymmetric stretch

Reaction Pathways for the Formation of $La(NHCH_2)$ and $La(NCH_3)$



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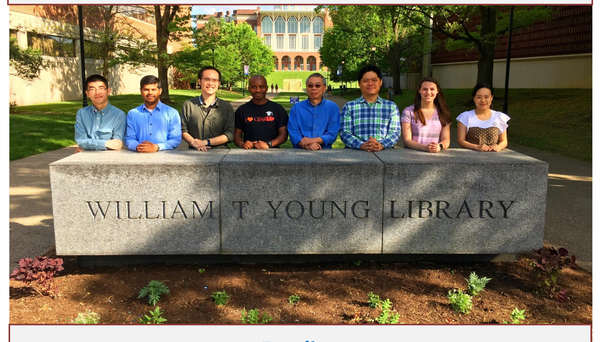

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