

STRESZCZENIE PRACY DOKTORSKIEJ: „Spectroscopy and photochemistry of astrophysically-relevant molecules of the cyanoacetylene family”

DOKTORANT: Urszula Szczepaniak

PROMOTOR: prof. dr hab. Robert Kofos;

KOPROMOTOR: dr hab. Claudine Crépin-Gilbert (Directrice de recherche au CNRS)

Data sporządzenia streszczenia w języku angielskim: 30.03.2017

This work is devoted to spectroscopic characterization and photochemical studies of several astrochemically interesting molecules of the cyanoacetylene family. The cryogenic rare-gas matrix isolation technique was employed for the preparation of most of the samples. Although rare gas matrices are not direct astrochemical analogues, they are transparent and non-reactive media that enable to study the interesting species.

Some of the molecules investigated, including $\text{CH}_3\text{C}_3\text{N}$ (and some of its isomers), $\text{CH}_3\text{C}_5\text{N}$, and HC_5N , were available *via* preparative organic chemical synthesis. Others appeared as the products of photochemical reactions run mostly in solid Kr in which the technique of UV-stimulated cryogenic elongation of unsaturated carbon-nitrogen chains was used to produce longer species. This approach led to successful preparation of HC_5N , starting from $\text{C}_4\text{H}_2 + \text{HC}_5\text{N}$, and C_{10}N_2 , starting from either $\text{C}_4\text{H}_2 + \text{HC}_5\text{N}$ or $\text{HC}_5\text{N} + \text{HC}_5\text{N}$. The method was further extended to the synthesis of methylated compounds with formation of $\text{CH}_3\text{C}_5\text{N}$ from $\text{CH}_3\text{C}_2\text{H} + \text{HC}_3\text{N}$, and $\text{CH}_3\text{C}_7\text{N}$ from $\text{CH}_3\text{C}_2\text{H} + \text{HC}_5\text{N}$. In addition, photochemical experiments using HC_5N -containing matrices led to the detection of HC_7N and of the C_5N^- anion. A general scheme describing the chain elongation processes was formulated.

Two isomeric products of the UV photolysis of Ar matrix isolated $\text{CH}_3\text{C}_3\text{N}$ were identified based on measured IR absorption spectra of pure compounds and on available theoretical predictions. The photochemical processes leading to their production have been described in terms of the precursor molecule being converted into propargyl cyanide, with allenyl cyanide formed as an intermediate.

A thorough spectroscopic characterization of gaseous, solid, and cryogenic matrix-isolated $\text{CH}_3\text{C}_5\text{N}$ was performed with the combined use of IR absorption, Raman scattering, electronic absorption, and electronic luminescence measurements. Phosphorescence of the related molecule, HC_5N , was revisited, and several new spectral assignments were reported.

Detection of $\text{CH}_3\text{C}_5\text{N}$, $\text{CH}_3\text{C}_7\text{N}$, HC_5N , C_{10}N_2 and C_5N^- as a result of UV-assisted chain elongation would not have been possible without these molecules possessing strong electronic phosphorescence, that was observed here for the first time. The vibronic structure of their emission and excitation was analysed, allowing characterization of several of their electronic states.

Similarities, differences, and patterns in selection rules, vibronic spacings, electronic transition energies, and phosphorescence decay times were examined for the homologous series HC_{2n+1}N , NC_{2n}N and $\text{CH}_3\text{C}_{2n+1}\text{N}$. Within each of these series, the $\tilde{a}-\tilde{X}$ vibrationless origin wavelengths were found to linearly correlate with the lengths of unsaturated carbon-nitrogen backbones. Extrapolation allows estimation of the $\tilde{a}-\tilde{X}$ vibrationless origin wavelength to currently unexplored cyanopolynes.