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“Theory and experiment in the spectroscopic research on astrochemically important nitriles and relevant molecules”

Abstract

The theoretical and experimental studies described in the Dissertation were conducted with the aim of broadening the knowledge on unsaturated nitriles, like cyanoacetylenes. These are one of the most important molecules detected in the interstellar medium, in circumstellar shells and in Titan's atmosphere. I have concentrated on chemical and spectroscopic properties, essential for the molecular astrophysics. "New", potentially astrochemical molecules were proposed. Those of importance for radio astronomy and for understanding the nature of diffuse interstellar bands were indicated.

Thermodynamic stability of $\text{HC}_5\text{N}$, $\text{C}_4\text{H}_2^+$, $\text{OC}_3\text{N}$, $\text{C}_6\text{H}_2^+$ was studied by ab initio calculations. Geometrical parameters and harmonic frequencies were predicted for the most stable isomers. High precision equilibrium rotational constants, vibration–rotation coupling constants, ground-state rotational constants, and anharmonic frequencies were calculated for $\text{OC}_2\text{NH}$, $\text{OCNH}$, $\text{OC(H)CN}$, $\text{OC(H)C}_2\text{H}$, $\text{C}_3\text{N}^-$, $\text{C}_5\text{N}^-$, as well as for the most stable isomers of $\text{HC}_3\text{N}$ and $\text{HC}_5\text{N}$. Some results could be compared to accessible experimental values. Precision of applied theoretical methods was estimated.

Excited electronic states of $\text{C}_3\text{N}^-$, $\text{C}_5\text{N}^-$, and of the isomers of $\text{HC}_3\text{N}$ and $\text{HC}_5\text{N}$ were investigated. Equilibrium geometrical parameters, harmonic frequencies, and excitation energies were predicted for the lowest electronic states of these molecules. Oscillator strength (for singlets states) and phosphorescence radiative lifetimes (for triplets states) were calculated. One of the cyanoacetylene isomers, namely $\text{C}_3\text{NH}$, is predicted to absorb visible light within the range of so far unidentified diffuse interstellar bands.

Theoretical calculations support the experimental identification of $\text{C}_3\text{N}^-$ and HCNC$_2$. These molecules were generated in electrical discharges (cold-window-radial-discharge technique; CWRD) through cyanoacetylene. The $\text{OC}_3\text{N}$ radical was tentatively identified in a noble gas matrix by infra-red absorption spectroscopy.

First results of the theoretical investigation on HMgNC and HMgCN molecules were reported. These open up a new research topic: the spectroscopy of astrochemically relevant organometallic nitriles.