

VUV photoionization of cyanoacetylene: towards a better characterization of the cation vibronic structure

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Cyanoacetylene, HC₃N, is the first member of the cyanopolyne family which exhibits two triple bonds of different nature (C≡C and C≡N). It presents a fundamental interest for the electronic structure of linear and extended π systems such as polyynes C_{2n}H₂ and cyanopolyynes HC_{2n+1}N. This molecule has been identified in the interstellar medium, in comets, and it is an important constituent of Titan's atmosphere. It can be photoionized in the upper atmosphere of this satellite where its cation contributes to the ionospheric chemistry. Few spectroscopic experimental studies have been performed on the cation electronic structure up to now [1-3] since this compound is not commercial and needs to be synthesized prior to any experiments.

To improve the spectroscopic knowledge of this important cation, high-resolution photoelectron studies have been performed using two vacuum-ultraviolet (VUV) radiation sources. Threshold-PhotoElectron Spectroscopy experiments have been carried out between 93000 and 175000 cm⁻¹ with the CERISES set-up on the DESIRS beamline of SOLEIL. New information has been assessed on the vibronic structure of HC₃¹⁴N⁺ cation and its ¹⁵N isotopologue with a typical resolution of 20 cm⁻¹, allowing to resolve for the first time the complex pattern of the B⁺ 2Π electronic state.

Different fragmentation channels consecutive to dissociative ionization have been observed and the corresponding appearance thresholds have been measured.

Complementary experiments have been performed with the VUV lasers of the CLUPS laser center of Paris-Sud University on two selected electronic states, X⁺ 2Π and B⁺ 2Π. Pulsed-Field Ionization Zero-Kinetic-Energy (PFI-ZEKE) photoelectron spectra have been recorded for the ¹⁴N and ¹⁵N isotopologues with a typical resolution of 2 cm⁻¹. Accurate values of the adiabatic ionization potential, of the spin orbit coupling constant and of vibrational mode energies of the X⁺ 2Π ground state have been determined.

All of these results are supported by complete active space second order perturbation theory calculations (CASPT2) performed by Jacky Liévin (ULB Brussels) to describe the multiconfigurational character of the excited electronic structure of HC₃N⁺.

REFERENCES

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