



## SEMINAIRE ISMO

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### **Isomerization, dissociation or growth ? On the photochemistry of some simple nitriles and of certain related, cryogenically isolated molecules**

Ever since the dawn of rare-gas matrix isolation, the technique demonstrates its potential in promoting discovery and/or detailed spectroscopic characterization of otherwise unstable molecules, including those of astrophysical significance. Unusual chemical species were shown to arise upon UV-stimulated isomerization of targeted precursors trapped between cryogenically immobilized inert atoms. Alternatively, irradiated parent species may permanently dissociate, often by losing a hydrogen atom or a proton. Furthermore (and rather surprisingly, given the rigidity of solid matrices), one may sometimes witness the molecular growth that proceeds *via* reactions between photolyzed precursors.

This presentation of selected examples, taken from our experience with simple nitriles, will start with the results concerning UV-irradiation of cyano- and dicyanoacetylenes in solidified rare gases, where all above-mentioned varieties of photochemical compartment could be observed. More recently, linear cyanopolyacetylenic chains as large as  $\text{NC}_{10}\text{N}$  or  $\text{HC}_9\text{N}$  were emerging *in situ* out of shorter cyanopolyacetylenic precursors isolated in solid krypton. Extending the backbone of analogue, methylated precursors was also possible. However, the photoisomerization of methylated cyanoacetylene (cyanopropyne) proceeded quite differently from that of cyanoacetylene. For instance, the anticipated isonitrile (isocyanopropyne) was not being formed at all. Such observations were rationalized on theoretical grounds.

It was of interest to juxtapose the known photochemistry of simplest nitriles with that of phosphalkynes, *i.e.* of the molecules featuring a  $-\text{CP}$  functional group. In the case of matrix-isolated phosphapropyne,  $\text{CH}_3\text{CP}$ , the observed processes were quite different, despite few similarities, from those reported for acetonitrile,  $\text{CH}_3\text{CN}$ . The final product is HCCP, a phosphinidene-type molecule (analogous to nitrenes or carbenes) that features a monovalent phosphorus atom and the electronic ground state of triplet multiplicity. The infrared spectrum of HCCP has been observed here for the first time. This phosphinidene is a probable interstellar molecule, given that HCCN and (tentatively) CCP were already observed in space. Further work, on photochemistry and spectroscopy of other phosphalkynes, including HCP and  $\text{HC}_3\text{P}$ , is under way, with participation of A. Lawzer and T. Custer and in collaboration with J.-C. Guillemin (ENSCR, Rennes) and C. Crépin (ISMO).

**Mardi 19 novembre 2019 à 11 h**  
**Amphithéâtre du bât 520 (3<sup>ème</sup> étage)**  
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