



Search for Missing Conformers: Matrix-Isolation SWAT

R. Fausto

*Department of Chemistry, University of Coimbra
P-3004-535 Coimbra, Portugal*

Spatial arrangements of atoms in a molecule, in particular molecular conformations and conformational flexibility, are the ultimate factor determining the qualities of the substances, from physical properties to chemical reactivity and biological activity. For substances where different conformational states may exist in equilibrium, the composition of the conformational mixture must then be precisely known in order to understand and predict their physicochemical behavior. On the other hand, since the chemistry of different conformers can be quite distinct (for instance, even simple molecules like formic acid, which has just two conformers, can react very differently depending on the conformation adopted by the molecule: the *cis* conformer photolyses preferentially to $\text{CO}_2 + \text{H}_2$, whereas the *trans* isomer reacts to yield mainly $\text{CO} + \text{H}_2\text{O}$ [1]), the possibility of changing, in an efficient and simple way, the conformational composition of a given chemical species, appears as a powerful tool to its fundamental study and can be forecast to have many possible practical uses.

Matrix-isolation FTIR spectroscopy has been shown to be one of the most powerful techniques to study molecular conformational preferences and also the specific properties of the different conformational forms. Different methods and strategies have been developed that give this technique nowadays unique capabilities for the conformational study of a substance. These include, for instance, the possibility of isolating a single conformer of a molecule which has several dozens of states significantly populated in the gas phase, and, contrarily to what happens if we try to achieve a similar result by crystallizing the compound, the unique conformer isolated in the cryogenic inert matrix and made available for spectroscopic examination is free of any strong intermolecular interaction [2]. Or, alternatively, the possibility of creating new conformational states, whose observation in other experimental conditions is practically impossible or extremely difficult to achieve [3,4].

In this lecture, I shall discuss some of the most effective approaches used in matrix-isolation FTIR spectroscopy to access elusive conformational species (Matrix-Isolation Special Weapons And Tactics, ☺) and provide several illustrative examples resulting from our own experience in this field of research.

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