

Keynote Lectures

[KN13] Single crystals on the move: Kinematic analysis of thermosalient and photosalient phenomena

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The central mechanistic feature of self-actuating biological systems are sensorial tissues that act as receptors to external stimuli and are coupled to actuating components that trigger locomotion by morphological changes. The underlying actuating components are usually composite structures based on kinematically active elements (e.g., oriented cellulose microcrystals in conifers) embedded in soft and flexible matrix that reshapes and modifies the macroscopic appearance of the plant. These hierarchical natural processes set an important mechanistic platform for the design of new biomimetic actuators. Among mechanically responsive materials, the few accidentally discovered examples of crystals which when heated suddenly jump, propelling themselves to distances that can reach thousands times their own size on a millisecond timescale provide probably the most impressive display of the conversion of light or heat into mechanical work. Such photosalient crystals and thermosalient crystals are biomimetic non-polymeric actuators par excellence. Due to the exclusivity and incongruity of this phenomenon, and also due to unavailability of readily analytical methodology for characterization, this colossal self-actuation has hardly aroused attention with chemists beyond the mere curiosity related to its visual appeal; any underlying mechanistic and structural aspects common for the materials capable of the phenomenon remain very poorly understood. We have recently embarked on detailed thermodynamic, kinematic and structural studies on mechanically responsive crystals, in order to arrive at an explanation for the reasons of the occurrence of this effect. The TS phenomenon is a kinematically complex, two-

stage process that occurs as five or six kinematic effects. It is fueled by a latent, sudden and rapid phase transition related by small but anisotropic cell expansion in crystals that are devoid of strong three-dimensional hydrogen bonding network. First, a conformational molecular transformation occurs whereby sufficient internal strain is accumulated, and the crystal is pre-stressed by buildup of internal pressure. Second, the strain is released by rapid structural transformation, resulting in crystal displacement. Either process in this two-stage mechanism poses conditions for occurrence (or absence) of the effect. According to the above discussion, the first event (crystal pre-stressing) is a necessary but insufficient condition for mechanical response. The time-scale on which the strain is released in the second stage (fast process) is critical to trigger self-actuation. Indeed, a mechanical response will occur only if the strain is released within a very short time interval; slow or gradual release of the accumulated strain translates into slow resizing/reshaping, deformation, or disintegration of the crystal devoid of notable mechanical motion. The detailed comparison of structural, thermodynamic and kinematic aspects of these organic martensites allows us to categorize the known TS materials into three classes:

(a) **Class I organic martensites:** This group includes flat, rigid molecules that pack in layers. A consistent feature of these molecules is the absence of extended hydrogen bonds; most of these molecules are devoid of groups capable of strong hydrogen bonding. These considerations indicate that the environment of all-weak intermolecular interactions is required to induce large molecular displacements during the structural transition in this group. Strong intermolecular interactions will absorb the strain in the crystal caused by heating, dampen the molecular displacement, and ultimately suppress the mechanical response.

(b) **Class II organic martensites:** This class contains bulky, flexible molecules decorated with multiple substituents on a central core.

The potential hydrogen bonding sites in these molecules are sterically hindered for strong intermolecular interactions by bulky groups.

(c) **Class III organic martensites:** this group contains molecules that saturate their hydrogen bonding potential by dimerization or polymerization. The phase transitions are sluggish, and the TS effect is weak.

Keywords: mechanical properties of crystals; phase transitions and structure; dynamic properties of solids