

Jack Saltiel's insightful mechanistic studies have earned him worldwide recognition as the foremost authority on cis-trans photoisomerization. Seminal contributions fall principally in four areas:

1. Mechanisms of olefin cis-trans photoisomerization.
2. Medium effects on the radiationless relaxation of electronically excited molecules.
3. Spin-statistical factors in diffusion-controlled reactions.
4. Factor analysis to resolve complex spectral matrices.

Area 4 advances the quantitative correlation of spectroscopic and photochemical observations, a unifying research theme. Studies of conformer specific photochemistry led to a new synthesis of vitamin D and studies of medium effects led to the discovery of bicycle pedal (BP) photoisomerization in solution, in glasses and in the solid state. Saltiel's discoveries have served as models for biological systems and have laid the foundation for theoretical advances.

Saltiel's singlet mechanism for stilbene isomerization, initially highly controversial, withstood the scrutiny of all transient spectroscopic advances. Credited for the use of the stilbenes as the prototypical cis-trans photoisomerization model, his work includes: (a) determination of deuterium and heavy atom substitution effects, (b) evaluation of torsional motions on excited state decay by studying rigid analogues, (c) mapping the energetics of central bond twisting in the triplet, ground and excited singlet states, (d) determination of temperature and structural effects on nonvertical triplet excitation transfer, (e) development of the medium enhanced barrier model for the separation of temperature and viscosity effects on excited state deactivation, and (f) basing microviscosity on diffusion coefficients to interpret torsional relaxation rate constants.

Saltiel established two bond and one bond photoisomerizations in 1,3-diene triplets and singlets, respectively. By elucidating the role of *s-cis*- and *s-trans*-1,3-diene triplets he provided a consistent interpretation of diene isomerization and dimerization responses to sensitizer triplet energy ("Saltiel plots"). He demonstrated the first quantum chain process, whereby triplet excitation transfer from diene to diene causes multiple isomerizations per photon and established allylmethylene geometries for diene triplets, as later confirmed by theory.

Naphthyl and anthryl group substitution for phenyl in stilbene and introduction of a second and third double bond between the two aryl groups led to the discovery of conformer specific adiabatic photoisomerizations and showed that, contrary to the popular Orlandi-Siebrand theoretical model, the 2^1A_g state plays no role in stilbene and diphenylpolyene photoisomerizations. Correlation of spectroscopic and photochemical observations in systems that adhere to Havinga's non-equilibration of excited rotamers principle was achieved by using principal component analysis and singular value decomposition with self-modeling (PCA-SM and SVD-SM) to resolve spectral matrices. This pioneering work unraveled a multitude of photophysical and photochemical responses including resolution of: (a) conformer spectra, (b) emissions from different excited states, and (c) complex fluorescence due to S_1 adiabatic reactions. Cardinal achievements are: *a priori* determination of model independent spectra of all intermediates in the bacteriorhodopsin (BR) photocycle and refutation of the widely accepted conclusion that previtamin D undergoes Hula-twist photoisomerization in glassy media. Analysis of fluorescence spectra obtained in the course of provitamin D photoisomerization required resolution of 7 spectral components! SVD-SM resolutions of the *s-cis*-1,3-butadiene UV spectrum, the delayed fluorescence of benzophenone, and the fluorescence spectrum of *all-trans*-1,6-diphenyl-1,3,5-hexatriene into *s-cis*- and *s-trans*-conformer spectra and the 2^1A_g and 1^1B_u spectra of the *s-trans*-conformer were achieved through compensation for nonlinear changes in spectra.



Saltiel's precise in depth studies have established a sound experimental scaffold for tests of theories as demonstrated by the plethora of theoretical papers that cite his work. His cis-trans photoisomerization studies are a universally important area of organic chemistry and photochemistry, influencing disciplines from vision to commercial vitamin D production to optical switches and other new and emerging photochemistry applications in materials science and biology. Continuous renewal of Saltiel's NSF proposals on the mechanisms of photochemical reactions since 1965 is a testament to the high regard his research enjoys.

A charter member of I-APS and the American Society for Photobiology (ASP), Saltiel has been a valued frequent, contributor to photochemical society meetings, Gordon Research Conferences and IUPAC Symposia as organizer and speaker. His contributions to the photosciences extend far beyond his laboratory. Saltiel credits scientific achievements in his lab to the efforts of able coworkers at all levels. Many students, who were introduced to research in his lab, have gone on to stellar careers. Examples are: (1) Mark Wrighton, formerly at MIT and currently Chancellor at Washington University, St. Louis, (2) Kirk Schanze, Professor, formerly at the University of Florida and now at UT, San Antonio, a past president of I-APS and I-APS Award winner and (3) Elizabeth Gaillard (Professor at the University of Northern Illinois), a past president of the American Society for Photobiology.